

STUDIES IN COMETARY ASTROPHYSICS

FINAL REPORT

15 April 1964 to 15 April 1965

Contract No. NASw-890

for

The National Aeronautics and Space Administration
Washington, D.C.

by

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FOREWORD

This final report contains the major results obtained from a laboratory study directed toward developing a better understanding of the chemical activity and phenomena of comets. This includes all the work that has been published or will soon be published. Some areas have not been included in this report because the status of the program has not progressed sufficiently for publication. These include electron and proton bombardment of low-temperature solids. The papers included in this report are:

- (1) Vacuum Ultraviolet Photolysis of Acetylene
- (2) Origin of the $C_2(A^3\Pi_g) \longrightarrow C_2(X^3\Pi_u)$ Emission in Comets
- (3) Vacuum Ultraviolet Photolysis of Hydrazine
- (4) Origin of $NH(A^3\Pi) \longrightarrow NH(X^3\Sigma^-)$ Emission in Comets
- (5) Vacuum Ultraviolet Photolysis of Mixtures of Methane and Water
- (6) The Chemistry of Comets--An Annotated Bibliography

The bibliography has been included since it was necessary to compile this information for our own program and it was felt that it would be of help to others interested in comets, cometary phenomena, or laboratory experiments pertinent to comets.

The Whipple comet model has been used as a basis for the laboratory research program. The most important aspect of this model is the postulation that a comet nucleus is a low-temperature solid containing large quantities of water, methane, and ammonia. The coma and tail are considered to be very low pressure gases. The energy environment for the comet is assumed to be the vacuum ultraviolet radiation from the sun and the energetic protons and electrons in the solar wind.

The laboratory investigations in cometary astrochemistry have resulted in obtaining information about the photochemistry of some simple molecules and their ability to produce excited free radicals. Our efforts have resulted in the production of C_2 from acetylene and the production of NH from hydrazine. The production of these radicals in their correct electronic state by decomposition of the appropriate compounds has not been demonstrated by previous investigators. In addition, the importance of reactions between $CO + OH$ and between $O + CH_4$ have been demonstrated in both low-temperature solids and gas-phase reactions. These systems could provide significant information about the reactions occurring at the coma-nucleus interface or in the nucleus itself.

It is expected that with further laboratory experiments and theoretical studies, cometary phenomena will become better understood. Areas requiring laboratory information include (a) quantitative primary decomposition mechanisms for simple and complex molecules absorbing photons or decomposing upon particle impact and (b) chemical and physical properties of low-temperature solids.

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marked To be submitted for publication.

SECTION 1

VACUUM ULTRAVIOLET PHOTOLYSIS OF ACETYLENE

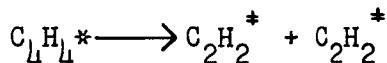
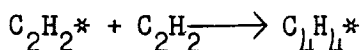
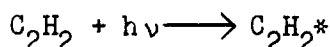
1. Vacuum Ultraviolet Photolysis of Acetylene

L. J. Stief, V. J. DeCarlo and R. J. Mataloni

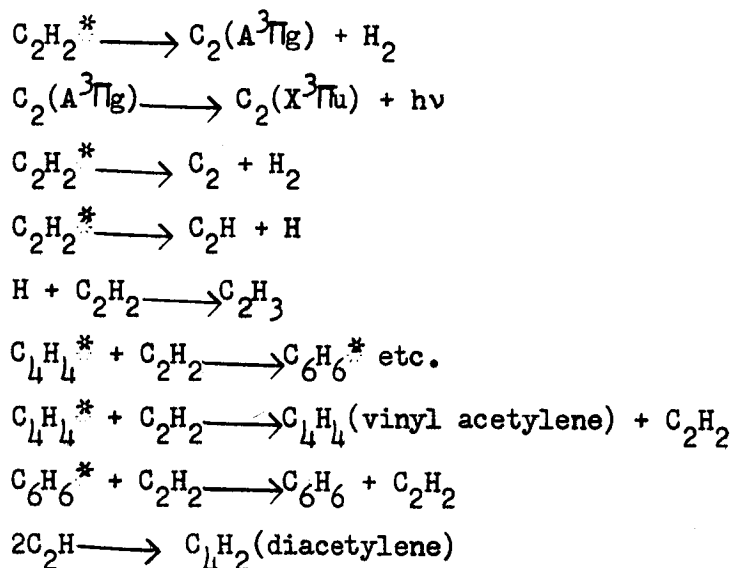
ABSTRACT

The vacuum ultraviolet photolysis of acetylene has been investigated at the krypton (1236\AA , 1165\AA) and xenon (1470\AA , 1295\AA) resonance lines. Evidence is presented for production of a long-lived excited state of acetylene. Decomposition of the excited state at low pressure leads to the formation of molecular hydrogen and excited C_2 . At the krypton resonance lines and at the 1295\AA Xe line, an emission consistent with Swan bands ($\text{A}^3\Pi_g \longrightarrow \text{X}^3\Pi_u$) of C_2 is observed at low pressures. No emission is observed in the photolysis of acetylene at 1470\AA . The intensity of the emission, the quantum yield for hydrogen production and the quantum yield for acetylene disappearance are all greatly reduced by the addition of a few millimeters of a quenching gas. Decomposition to H_2 and C_2 also occurs in the solid phase.

The overall photolysis is explicable in terms of an excited molecule mechanism in which the formation of C_2 in excited $\text{A}^3\Pi_g$ state depends on the energy of the incident photon:



Note: This section, under the above title, is now in press, J. Chem. Phys. (1965)



1.1 Introduction

The direct photolysis of acetylene at 1849\AA has been investigated by Zelikoff and Aschenbrand.¹ Earlier work on both the direct photolysis and on the mercury-photosensitized reactions of acetylene has been reviewed by Steacie.² In the direct photolysis at 1849\AA , it was concluded that both free radicals and excited acetylene molecules were involved in the photochemical decomposition. This is consistent with the absorption spectrum³ in that a continuum with superposed bands from 1550\AA to 2000\AA exists. The products of the photolysis were found to be a polymer which resembled cuprene, hydrogen, ethylene, diacetylene, vinyl-acetylene and benzene.

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1. M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys. 24, 1034 (1956).
 2. E. W. R. Steacie, Atomic and Free Radical Reactions, Reinhold, New York, 1954.
 3. T. A. Nakayama and K. Watanabe, J. Chem. Phys. 40, 558 (1964).

In the banded region below 1550\AA , the only information available states that diacetylene, vinylacetylene, benzene, polymer, and very small amounts of hydrogen are formed subsequent to photolysis⁴ at 1470\AA .

In this investigation the photolysis of acetylene has been examined at the krypton and xenon resonance lines and at low pressures of acetylene. Under these conditions, deactivation of excited molecules or of excited molecular fragments is reduced. This should lead to information concerning the decomposition of excited molecules and possibly to the observation of emission from excited species. Thus, the vacuum ultraviolet photolysis of ethane, ethylene, and acetylene has been examined at low pressures for the possible production of excited C_2 . Emission was observed from acetylene, but not from ethane or ethylene. Consequently, an investigation of the photochemistry of acetylene at low pressure seemed desirable, and such an investigation forms the basis for this communication.

1.2 Experimental

Light Source and Actinometry

The xenon and krypton resonance lines were excited in an air-cooled electrodeless discharge operated by a Raytheon 2450-Mc microwave generator. The design and construction of the lamps as well as the effect of various dimensions on the intensity are given elsewhere.⁵ The lamps were filled with 1 mm of the pure gas and the side arm was cooled with

4. I. Tanaka and J.R. McNesby, unpublished work.

5. L. J. Stief and R. J. Mataloni, to be published.

liquid nitrogen for the krypton lamp and with liquid oxygen for the xenon lamp. The krypton resonance lamp emits radiation at 12360\AA (10 eV or 231 kcal/einstein) and at 11650\AA (10.6 eV or 245 kcal/einstein). The intensity of the latter line is weak, amounting to less than 20% of the 12360\AA line. The rate data were not considered to be sufficiently accurate to warrant correction for absorption at 11650\AA in calculating quantum yields. The xenon resonance lamp emits radiation at 14700\AA (8.4 eV or 195 kcal/einstein) and at 12950\AA (9.6 eV or 221 kcal/einstein). The intensity of the latter is about 2% of that for the 14700\AA line and, except for one experiment noted in the results, has not been taken into consideration.

The lamps were normally operated with freshly polished LiF windows attached with Apiezon-W wax, epoxy cement, or a Ag-AgCl seal. For new lamps, the emission spectra contained many impurity lines in the region of 16500\AA and above. The impurity lines decreased, however, with operation of the lamp. A typical krypton lamp, after a few hours use, had no photochemical effect on carbon dioxide or acetylene, each of which was contained in a cell fitted with a sapphire window. This indicates that no effective radiation above 14500\AA was emitted by the lamp. Photolysis of CO_2 using a xenon lamp resulted in formation of CO, showing that wavelengths above 14500\AA were indeed transmitted. Light intensities, calculated from the yield of CO from CO_2 photolysis,^{6, 7} assuming $\Phi_{\text{CO}} + 1$, were usually between 10^{15} and 10^{16} quanta/sec.

6. B. H. Mahan, *J. Chem. Phys.* **33**, 959 (1960).

7. P. Warneck, *Disc. Far. Soc.*, No. **37**, p. 57 (1964).

Materials

Acetylene $-d_2$ was obtained from Merck & Co., Montreal, Canada, and contained less than 2% C_2H_2 plus C_2HD . Infrared analysis of a typical sample of C_2D_2 indicated that absorption due to C-H stretching, if present, amounted to less than 2% of the absorption due to C-D stretching. The acetylene was obtained from the Matheson Co., Inc., East Rutherford, N.J., and had a stated minimum purity of 99.6% acetylene. Several distillations in vacuo from a trap at $-78^\circ C$ to one at $-196^\circ C$ were performed in order to remove traces of acetone, as the acetylene is dissolved in acetone for shipment in cylinders. Mass spectrometric analysis did not indicate any impurities above the stated level. Krypton, xenon, and carbon dioxide were obtained from the Air Reduction Company, Jersey City, N.J. The known impurities were 150 ppm Xe in the krypton and 22 ppm N_2 plus less than 20 ppm Kr in the xenon. The nitrogen and oxygen (Research Grade) and the nitric oxide (99% minimum purity) were obtained from Matheson. Nitrogen was removed from nitric oxide by continued thawing and pumping on a sample maintained at $-210^\circ C$. Nitric oxide was always admitted to the reaction vessel from a trap maintained at $-183^\circ C$ to prevent contamination from other oxides of nitrogen.

Procedure

A mercury-free Pyrex reaction vessel of 458 cc volume and having an absorption path of approximately 15 cm was fitted with a 25 mm diameter LiF entrance window at right angles to a 25 mm diameter quartz exit window. The windows were sealed to the reaction vessel with Apiezon-W wax or epoxy cement. Two horn-shaped light traps were incorporated in the cell,

one directly opposite each window. The vacuum system was also mercury-free and stopcocks were greased with Apiezon-N grease. Pressures were measured in the reaction cell with a CVC autovac gauge which had been calibrated against a Trans-Sonics capacitance manometer for each gas used.

The 25 mm diameter LiF window of the rare gas resonance lamp was butted against the LiF entrance window of the reaction cell. The intensity of light absorbed in the cell was not enhanced by blowing helium gas past the windows, indicating that little or no light was absorbed in an air gap between the two LiF windows. The entrance slit of an f/3.5 Bausch & Lomb grating monochromator (#33-86-25, 3500Å to 8000Å, reciprocal linear dispersion 64Å/mm, blazed at 5000Å) was placed at the exit window of the reaction cell with a 1P21 phototube operated from an Aminco microphotometer at the exit slit of the monochromator.

The emission was recorded on the microphotometer as percent transmission. Scattered visible light from the resonance lamp, which amounted to only a few percent of the level of emission from acetylene, was subtracted from the observed total emission. Readings were taken at various pressures and at wavelength settings in a random order to eliminate any possible effect due to the photodecomposition of acetylene with time. Due to the faintness of the emission, one millimeter was the smallest slit opening on the monochromator that could be used.

In the experiments where the production of hydrogen and the disappearance of acetylene were studied, the pressure of hydrogen in the reaction cell was measured at several time intervals with the rate obtained

from the linear portion of the pressure vs. time plot. Acetylene pressure was measured at the beginning and at the end of the experiment. The only gas formed in the reaction was hydrogen which is noncondensable at the liquid nitrogen temperature, and samples were taken for isotopic analysis in a CEC 21-130 mass spectrometer by expansion of the gas into a sample bulb with a volume which was approximately the mean of the volume of the reaction cell and the expansion volume of the spectrometer.

The photolysis of solid acetylene was performed using an all-glass Dewar with a 25 mm LiF window directly opposite a deposition surface. Acetylene was deposited through a 2 mm ID nozzle for a period of about 15 minutes. The hydrogen produced during photolysis was measured at various time intervals in the Dewar cell which had a volume of 585 cc.

1.3 Results

Spectroscopic Observations

A broad, structureless emission in the region $4000\overset{\circ}{\text{\AA}}$ to $6500\overset{\circ}{\text{\AA}}$ is observed when acetylene vapor is photolyzed at the krypton resonance lines. The spectrum obtained at 25°C and $56\text{ }\mu\text{ Hg}$ pressure is shown in Figure 1-1. The entire spectrum has been recorded at pressures from $2.8\text{ }\mu$ to 7.8 mm Hg . The same broad emission was observed at all pressures with the maximum intensity at $5000\overset{\circ}{\text{\AA}}$ in each case. The effect of acetylene pressures in this range on the relative intensity of the emission at $5000\overset{\circ}{\text{\AA}}$ is seen in Figure 1-2. The maximum in the intensity of the emission occurs at $56\text{ }\mu\text{ Hg}$, with a rather sharp decrease at both lower and higher pressures.

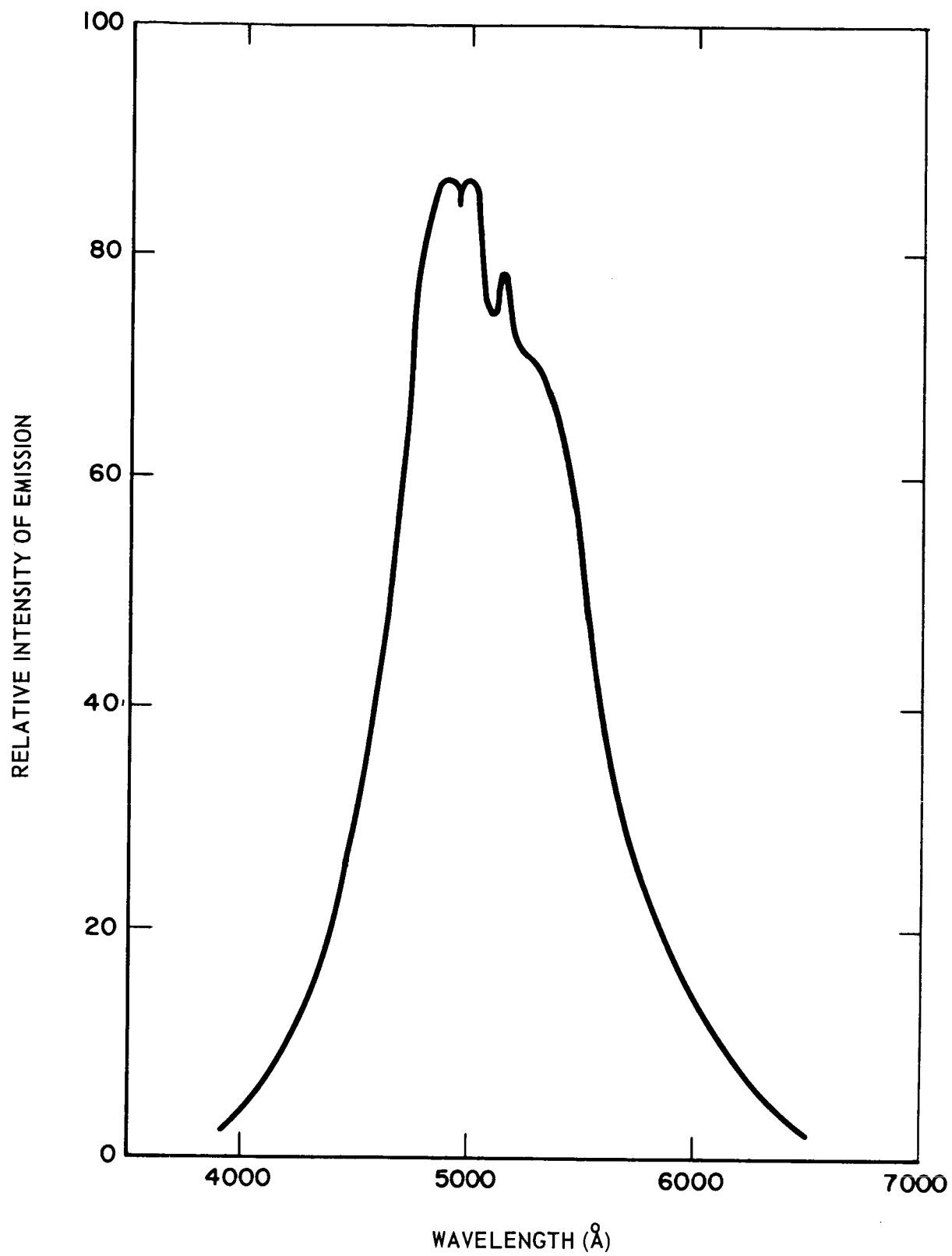


Figure 1-1. Emission Spectrum Observed During Photolysis of Acetylene at 1236 Å and 56 μ Hg Pressure

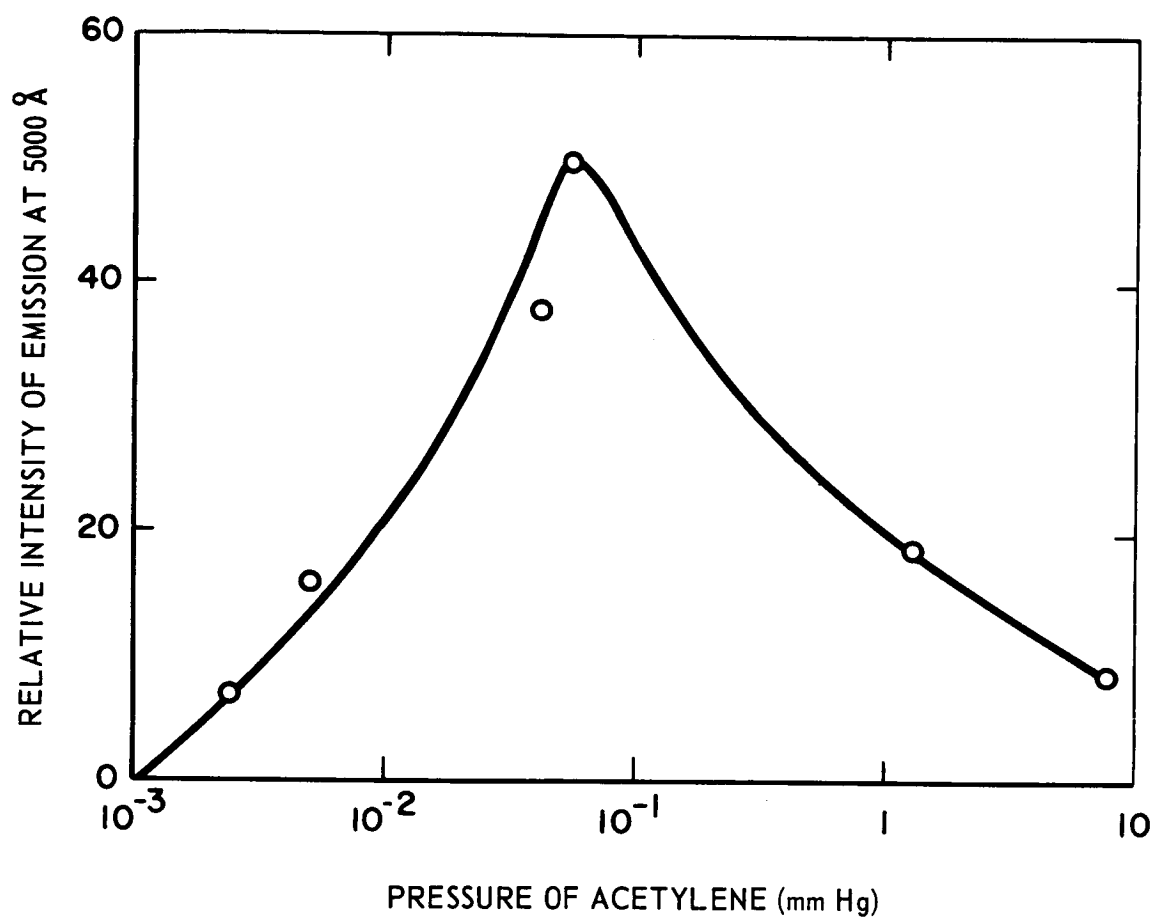


Figure 1-2. Effect of Pressure of Acetylene on Intensity of Emission at 5000Å
Observed During Photolysis of Acetylene at 1236Å

The increase in intensity of the emission in the pressure range $1\ \mu$ to $50\ \mu$ Hg is probably attributable to increased absorption of light by the acetylene. The decrease in the intensity of the emission with pressure in the region above $56\ \mu$ Hg is discussed in the next section in terms of the effect of pressure on the overall photochemical decomposition.

When acetylene is photolyzed at the xenon resonance lines (1295\AA and 1470\AA), a weak emission in the region 4000\AA to 6500\AA is observed, the intensity of which is only a few percent of that for emission observed in the photolysis at the krypton resonance lines (1165\AA and 1236\AA). Since the 1295\AA line amounts to only a few percent of the 1470\AA line in the xenon resonance lamp, the possibility exists that the emission is due entirely to absorption of the 1295\AA line. To test this, acetylene was exposed to radiation from a xenon resonance lamp when the LiF window on the reaction cell was replaced by a sapphire window. Despite the fact that the CO_2 could be decomposed in such a cell, showing that the 1470\AA line was indeed transmitted, no emission was detected from acetylene. This is taken as evidence that photons of $8.4\ \text{eV}$ are not capable of producing the emission from acetylene, but that photons of $9.6\ \text{eV}$ or greater energy are capable of so doing.

The effect of the addition of nitrogen and oxygen upon the intensity of the emission is shown in Figure 1-3, along with the effect of additional acetylene. The cell originally contained $56\ \mu$ acetylene and the pressure was increased by adding nitrogen, oxygen, or acetylene. It may be seen that all three gases are essentially equally effective in quenching the emission, and that the intensity of the emission is quickly reduced to a

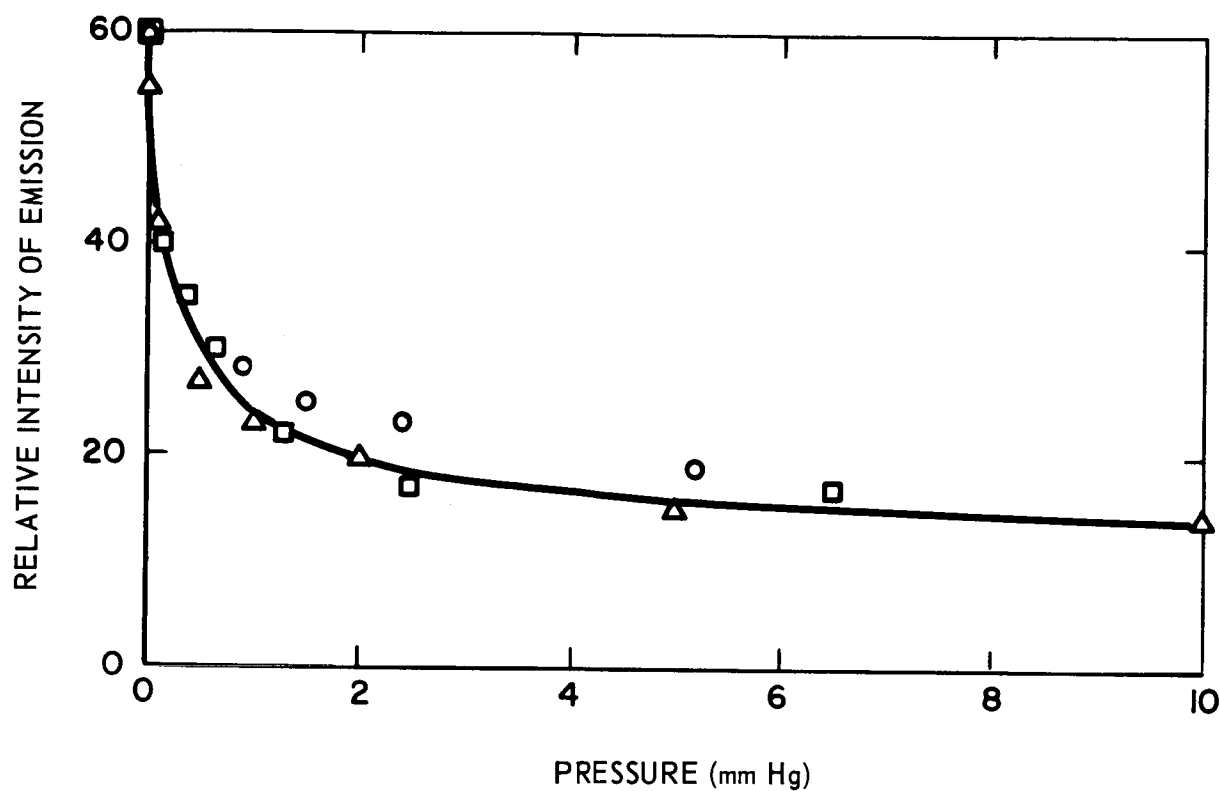


Figure 1-3. Effect of Oxygen (O), Nitrogen (Δ), and Acetylene (\square) on the Intensity of the Emission Observed During Photolysis of Acetylene at 1236Å

low value by addition of a few millimeters of a quenching gas with no further quenching evidenced by continued increase in pressure.

The emission observed from acetylene-d₂ upon photolysis at the krypton resonance lines is indistinguishable from that observed from acetylene under our experimental conditions.

Attempts to photograph the emission using a Hilger-Watts E517 spectrograph were frustrated by decomposition of acetylene and by deposition of polymer on the entrance window of the reaction cell. Experiments with up to twenty-hours exposure on Kodak 103a0 or 103aF plates with replacement of the LiF entrance window every two hours failed to result in observation of any structure in the emission.

Hydrogen Formation

In the pressure region of 50 μ where the emission is most intense, photolysis of C₂D₂ results in the formation of D₂, HD, and H₂. Both mass spectrometric and infrared analysis of the C₂D₂ indicate that the sample is at least 98% deuterated. Hence, the formation of HD and H₂ probably results from the presence of water vapor which is absorbed on the walls of the photolysis cell or the vacuum system and which is subsequently photolyzed and/or exchanges with the deuterated acetylene. The effect is much less evident at higher pressures of acetylene where less H₂ and little or no HD is formed. Also, the amount of D₂ present in the hydrogen formed in the photolysis of acetylene-d₂ is lower (40%) when photolysis is performed in a new reaction vessel than it is (64%) when photolysis is performed under otherwise identical conditions in a vessel that has been

evacuated and in use for some time. Distillation of acetylene- d_2 from a trap at -80°C , use of a break seal instead of a stopcock to isolate the reaction cell, and heating of the reaction cell to 300°C for prolonged periods with continued evacuation to 10^{-6} mm Hg were all tried without success in an effort to suppress formation of H_2 and HD.

In view of this, all results on the production of hydrogen from acetylene are based on the measurement of D_2 from the photolysis of C_2D_2 . This gives a minimum value for the quantum yield of hydrogen production. Quantum yields are based on intensity measurements using CO_2 as an actinometer.^{6 7} The CO_2 was photolyzed in the same cell used for acetylene photolysis and intensity measurements were made immediately before and immediately after photolysis of the acetylene sample. Plots of the amount of CO from CO_2 photolysis at 10 mm Hg are linear with time up to at least 15 minutes.

In the photolysis of 56μ of C_2D_2 at the xenon and at the krypton resonance lines, the quantum yield for hydrogen formation is 0.07 in both instances (Table 1-1). Corrections were made for the fraction of light absorbed by carbon dioxide⁶ and acetylene,³ respectively, based on their absorption coefficients at 1470\AA and 1236\AA . Measurements of relative absorption at 1236\AA by C_2H_2 and C_2D_2 in the same absorption cell indicate that the absorption coefficient for the deuterated compound does not differ by more than 10% from that of the nondeuterated compound. This is to be expected if absorption is associated with the carbon-carbon triple bond. In the case of ethylene,⁸ the absorption coefficients of C_2H_4 and C_2D_4 have

8. M. C. Sauer and L. M. Dorfman, J. Chem. Phys. 35, 497 (1961).

TABLE 1-1

EFFECT OF WAVELENGTH ON HYDROGEN PRODUCTION AND ACETYLENE
DISAPPEARANCE IN PHOTOLYSIS OF ACETYLENE AT 56 μ Hg PRESSURE

	1236 ⁰ \AA	1470 ⁰ \AA
lamp int. $\times 10^{-15}$ (quanta/sec)	3.90	2.71
% absorption	10	18
Ia $\times 10^{-14}$ (quanta/sec)	3.90	4.88
R _{D₂} $\times 10^{-14}$ (molecules/sec)	0.26	0.34
Φ_{D_2} (molecules/quantum)	0.07	0.07
R _{-C₂D₂} $\times 10^{-14}$ (molecules/sec)	0.65	0.81
$\Phi_{-C_2D_2}$ (molecules/quantum)	0.17	0.17
$\Phi_{-C_2D_2} / \Phi_{D_2}$	2.4	2.4

been shown to be indistinguishable at 1470\AA and absorption is to be attributed to the carbon-carbon double bond. Other data lacking, the absorption coefficients for acetylene³ were used to calculate absorption by C_2D_2 .

The effect of pressure of acetylene on the production of hydrogen is shown in Table 1-2. Plots of hydrogen pressure are linear with time up to 60 minutes for experiments at $56\ \mu$ only. For the $112\ \mu$, $180\ \mu$, and $2.4\ \text{mm Hg}$ experiments, the rate of hydrogen production is taken from the initial slope of the pressure vs. time curve (Figure 1-4). Polymer formation, which is quite evident at the highest pressure ($2.4\ \text{mm}$) results in decreased transmission of radiation and, hence, decreased production of hydrogen with time. The percent decomposition was high (about 30%) for the latter experiment, but the amount of light absorbed in the system dropped by only 3% (from 100% to 97%) as a result of the drop in acetylene pressure. For the $112\ \mu$ and $180\ \mu$ experiment, however, the amount of light absorbed is low (19% and 30%, respectively) and, for the same percentage decomposition (30%) as at $2.4\ \text{mm}$ pressure, the drop in acetylene pressure results in a considerable fractional decrease in the amount of light absorbed. The gradual curvature of the pressure vs. time plots for $112\ \mu$ and $180\ \mu$ experiments are thus attributed to change in acetylene pressure while the more drastic effect noted for the $2.4\ \text{mm}$ experiment is explained on the basis of extensive polymer formation. This conclusion is further supported by the fact that absorbed intensities in the reaction cell, as determined by CO_2 actinometry, were the same to within 5% before and after the low pressure photolysis while the performance

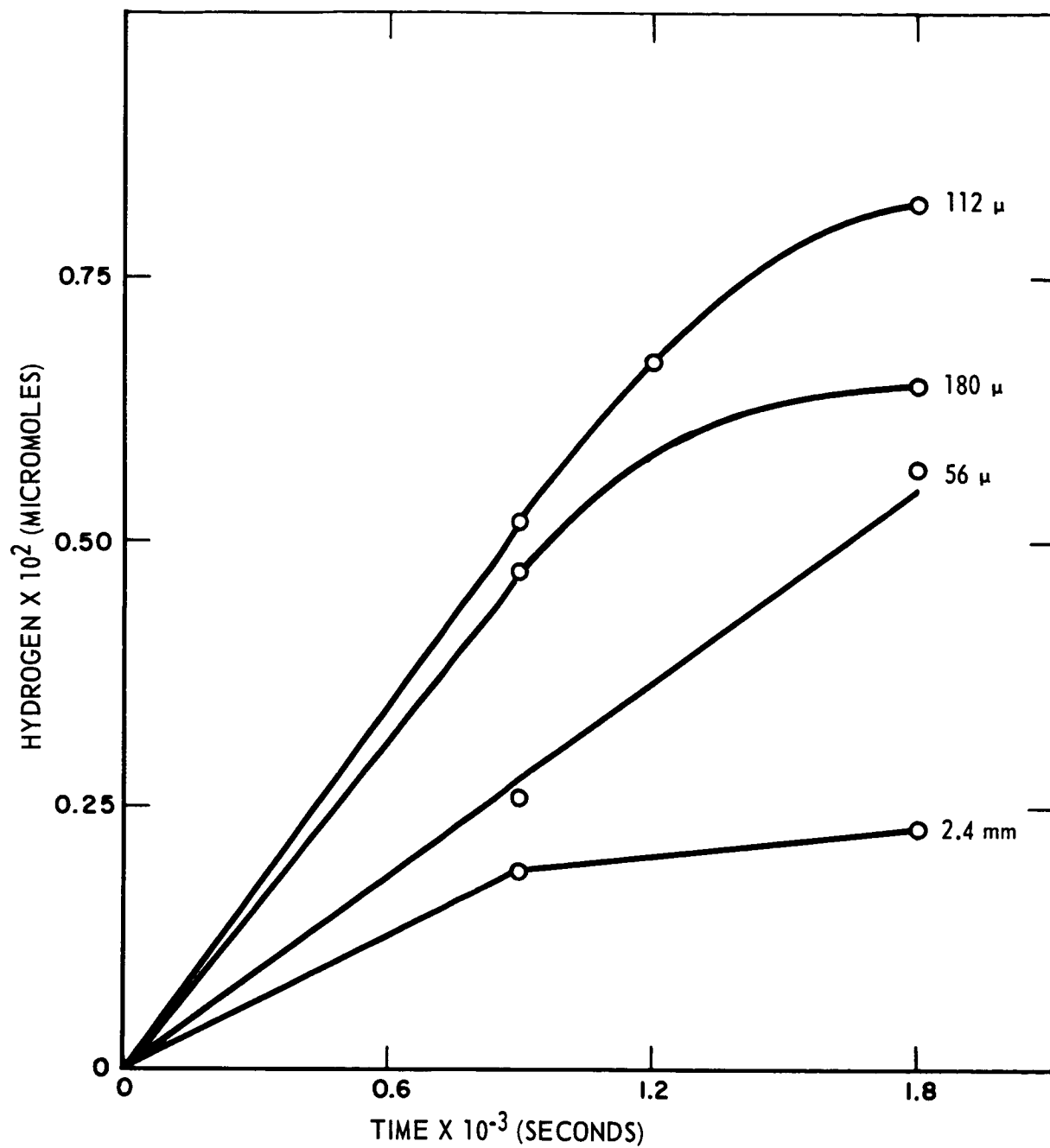


Figure 1-4. Time Dependence of Hydrogen Production in the Photolysis of Acetylene at 1236 Å

TABLE 1-2

EFFECT OF PRESSURE OF ACETYLENE ON HYDROGEN PRODUCTION AND
ACETYLENE DISAPPEARANCE IN THE PHOTOLYSIS OF ACETYLENE AT 1236 \AA

	Pressure of Acetylene				
	56 μ	112 μ	112 μ	180 μ	2400 μ
lamp int. $\times 10^{-15}$ (quanta/sec)	8.10	8.10	7.17	7.64	3.90
% absorption	10	19	19	30	100
Ia $\times 10^{-14}$ (quanta/sec)	8.10	15.4	13.6	22.9	39.0
R _{D₂} $\times 10^{-14}$ (molecules/sec)	0.79	2.01	1.93	1.90	0.82
ϕ_{D_2} (molecules/quantum)	0.10	0.13	0.14	0.08	0.02
R _{-C₂D₂} $\times 10^{-14}$ (molecules/sec)	1.59	4.83	n.d.	8.09	~35
$\phi_{-C_2D_2}$ (molecules/quantum)	0.20	0.31	n.d.	0.35	~ 1
$\phi_{-C_2D_2} / \phi_{D_2}$	2.0	2.3	n.d.	4.2	~50

n.d. = not determined

of a 2.4 mm photolysis experiment resulted in decrease in absorbed intensity by a factor of 40. Cleaning or replacement of the window results in recovery of the original transmission. The use of initial slopes of pressure-time curves means that rates of hydrogen production are estimated in regions where 10-15% of the acetylene has reacted and where accumulation of polymer is minimized.

Since the low quantum yield observed at 2.4 mm acetylene may be suspect because of polymer deposition on the entrance window, the effect of 2 mm CO_2 on the production of hydrogen in photolysis of acetylene at 56 μ Hg pressure was examined. The result shows that the quantum yield of D_2 is reduced by a factor of 5 (Table 1-2) or 15 (Table 1-3) when the added gas is acetylene or carbon dioxide, respectively. To test the possibility that oxygen atoms, formed in the photolysis of CO_2 , could react with molecular hydrogen after the latter had been formed in photolysis of acetylene, a mixture of hydrogen and CO_2 (the same amounts as in the C_2H_2 - CO_2 experiment) was photolyzed for an hour. No loss of molecular hydrogen occurred in the process.

When 56 μ NO is added to 56 μ C_2D_2 (Table 1-3), the quantum yield for hydrogen formation is reduced from 0.1 to 0.006. This is based on the amount of light absorbed by the acetylene only (10%) and neglects the absorption by NO (6%).

Photolysis of C_2H_2 deposited at -196°C at the krypton and xenon resonance lines results in the production of hydrogen. Plots of pressure of hydrogen formed vs. time are linear for photolysis times up to three hours

TABLE 1-3

EFFECT OF ADDED GASES ON HYDROGEN PRODUCTION AND
ACETYLENE DISAPPEARANCE IN PHOTOLYSIS OF 56μ ACETYLENE AT 12360\AA

	Added Gas			
	None	CO ₂	N ₂	NO
Pressure added gas (mm Hg)	--	2.0	2.0	0.056
Intensity of lamp x 10^{-15} (quanta/sec)	8.10	1.07	10.8	1.15
% absorption by C ₂ D ₂	10	10	10	10
% absorption by added gas	--	12	nil	6
ϕ_{D_2} (molecules/quantum)	0.10	0.006	n.d.	0.006
$\phi_{-C_2D_2}$ (molecules/quantum)	0.20	n.d.	0.01	n.d.

n.d. = not determined

(Figure 1-5). Although the amount of light absorbed in the system is unknown, the rate of production of hydrogen in the photolysis of solid acetylene is about 10% of that observed from gas-phase photolysis at 2.4 mm pressure. The rate of production of hydrogen does not appear to be strongly dependent on the wavelength of light employed, but the rate is somewhat higher when a larger sample is deposited. Photolysis of C_2D_2 deposited at $-196^\circ C$ results in formation of D_2 with small amounts of H_2 and HD also observed. Extensive polymer formation is also observed in the photolysis of solid acetylene.

Acetylene Disappearance

The amount of acetylene remaining at the end of the gas-phase photolysis was measured and its purity checked in the mass spectrometer. Since the rate of disappearance of acetylene was not determined from the initial slopes of pressure vs. time plots as for hydrogen production, quantum yields quoted for acetylene disappearance represent minimum values and are not as accurate as quantum yields for hydrogen formation. At 56μ for photolysis at both the xenon and krypton resonance lines, $\Phi_{-C_2D_2}$ is 0.17 (Table 1-1), i.e., about 20% of the absorbed quanta results in decomposition of acetylene under these conditions. The quantum yield for acetylene disappearance increased somewhat at 112μ and again at 180μ , but increases very markedly to a value near unity at 2.4 mm pressure of acetylene (Table 1-2). Since the absorbed intensity decreased by a factor of 40 for the latter experiment due to polymer deposition, an attempt was made to correct for this on the assumption that the intensity decreased linearly with time. No correction

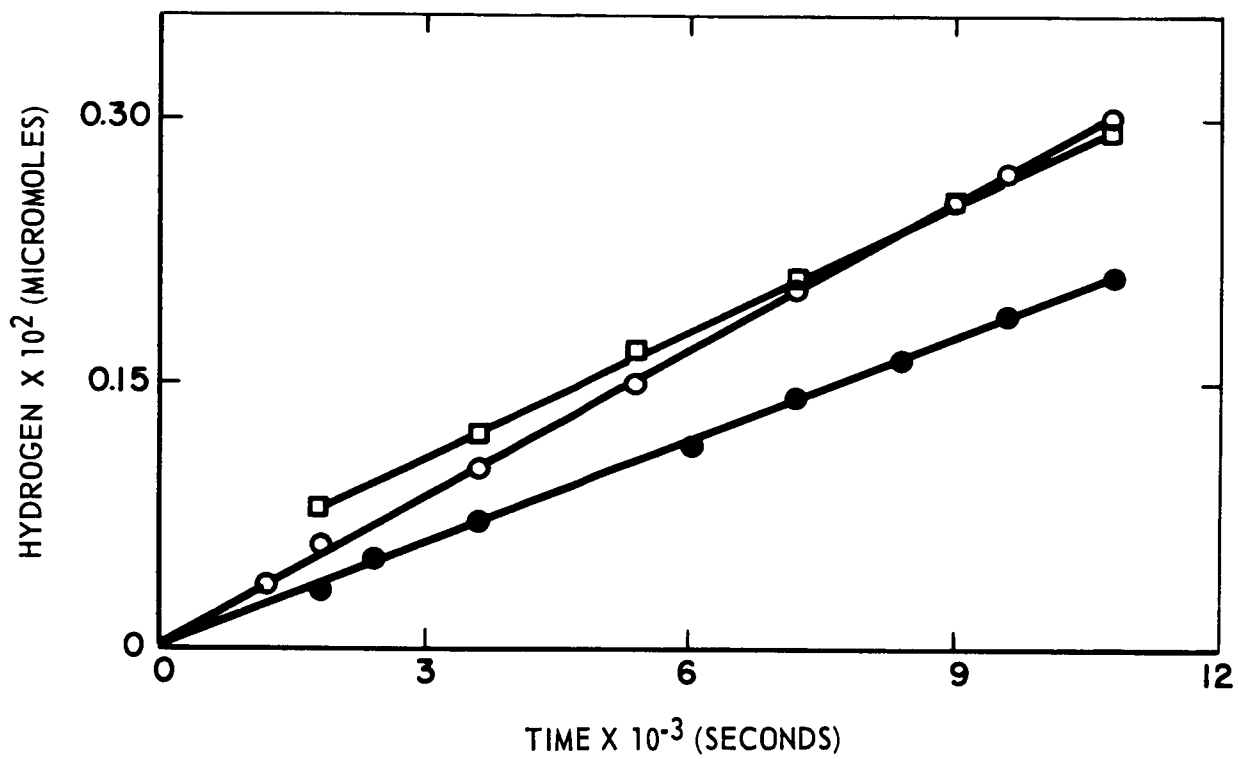


Figure 1-5. Time Dependence of Hydrogen Production in the Photolysis of Acetylene Deposited at -196°C

was made for the 112 μ and 180 μ experiments to compensate for decreased absorption of light due to continual decomposition of acetylene. When 56 μ of acetylene is photolyzed in the presence of 2 mm N_2 , (Table 1-3) the quantum yield for acetylene disappearance is reduced to 0.006, i.e., acetylene decomposition is almost negligible in the presence of a few millimeters of an inert gas.

1.4 Discussion

Evidence for Long-Lived Excited State of Acetylene

The vibrational structure exhibited in the vacuum ultraviolet absorption spectrum of acetylene³ suggests that the electronically excited acetylene formed by initial absorption of light (Reaction 1)



may have a relatively long lifetime with respect to dissociation. It can be concluded that the excited state of acetylene formed upon absorption of a photon of energy 10 eV is sufficiently long-lived to experience collisions with other molecules in the gas phase (Reaction 2) or, at very low pressures, collision with the wall of the reaction vessel.



This conclusion is supported by the following observations made in this investigation. First, the fact that the quantum yield for the disappearance of acetylene is as low as 0.2 in the 50 μ pressure region means that 80% of the excited acetylene molecules lose their energy and return to ground state by collision with normal acetylene molecules or by collision with the walls.

In the 50 μ pressure region, collisional deactivation of excited acetylene probably proceeds by a chemical mechanism in which an excited dimer¹ is formed



and dissociates into two acetylene molecules



containing the original electronic excitation energy in the form of internal energy which is inadequate to promote further chemical reaction. Collisional deactivation at the walls cannot be excluded since in the 50 μ pressure region, the frequency of collisions with the wall is of the same order of magnitude as the frequency of collisions with molecules in the gas phase. Secondly, in the presence of 2 mm of nitrogen, the quantum yield for acetylene disappearance is reduced to 0.006. This suggests that essentially all of the excited acetylene molecules are quenched by collision with nitrogen molecules at this pressure and little or no decomposition occurs. Finally, the fact that the quantum yield for disappearance of acetylene increases from 0.2 to about unity and that polymer formation is enhanced with an increase in acetylene pressure indicates that excited acetylene lives long enough to collide with ground-state acetylene; this results in polymer formation and increased disappearance of acetylene. Polymer formation has been explained in terms of excited molecules in the direct photolysis of acetylene¹ at 1849 \AA as well as in the mercury-sensitized reaction.² It may also be noted that Lichten⁹ has detected a metastable state of acetylene

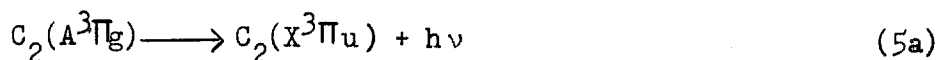
9. N. Lichten, J. Chem. Phys. 32, 2152 (1963).

produced by electron bombardment. This metastable state lies about 8.5 eV above ground and has a lifetime of the order of a fraction of a millisecond.

Decomposition of Electronically Excited Acetylene

The emission observed (Figure 1-1) in region 4000-6000Å when acetylene vapor is subject to irradiation at the krypton resonance lines and at the 1295Å Xe line is consistent with the Swan system ($A^3\Pi_g \longrightarrow X^3\Pi_u$) of C_2 . The band heads are located at 4383Å (2,0), 4737Å (1,0), 5165Å (0,0), 5636Å (0,1), and 6191Å (0,2) for this system,¹⁰ with the band at 5165Å being the strongest. The fact that D_2 is observed as a product in the photolysis of C_2D_2 suggests that hydrogen is formed in a molecular elimination process since hydrogen atoms, if formed, would be removed by addition to acetylene rather than abstract to form hydrogen. This is analogous to the situation in the photolysis of ethylene.⁸

Thus, both spectral observations and product analysis are consistent with the occurrence of the primary decomposition process, (Reaction 5) followed by decay of excited C_2 with emission of the Swan bands (Reaction 5a).



Formation of molecular hydrogen and of C_2 in some electronic state lower than the $A^3\Pi_g$ state, such as the $x^1\Sigma_g^+$ ground state¹¹ or the low lying

10. G. Herzberg, Spectra of Diatomic Molecules, Van Nostrand, N.Y., 1950.

11. E. A. Ballik and D. A. Ramsay, J. Chem. Phys. **31**, 1128 (1959).

(1.6 kcal/mole) $x^3\Pi_u$ state, probably also occurs, since, at 1470\AA , hydrogen was observed to be produced with the same quantum yield as for the shorter wavelengths while no emission is observed under these conditions.



The energetics of Reactions (5) and (6) are summarized below:

<u>Product</u>	<u>ΔH kcal/mole</u>	<u>Wavelength below which process is energetically possible</u>
$\text{C}_2(x^1\Sigma_g^+)$	145	1971\AA
$\text{C}_2(A^3\Pi_g), v = 0$	200	1429\AA
$\text{C}_2(A^3\Pi_g), v = 2$	210	1361\AA

For Reaction 6, ΔH was estimated using 54 kcal/mole for the heat of formation of acetylene¹² and 199 kcal/mole for the heat of formation of ground state C_2 . The heat of formation of C_2 was estimated using 170 kcal/mole for heat of sublimation of carbon¹³ and 141 kcal/mole for dissociation energy¹⁴ of C_2 . The total excitation of the zero vibrational level of the $^3\Pi_g$ state (origin of 0,0 band at 5165\AA) was taken as 55 kcal/mole while that for the second vibrational level (origin of 2,0 band at 4383\AA) was taken as 65 kcal/mole.

-
12. A. G. Gaydon and K. S. Wolfhard, Flames-Their Structure, Radiation and Temperature, Chapman and Hall, London, 1960.
 13. D. M. Kern, J. Chem. Ed. **33**, 272 (1956).
 14. E. A. Ballik and D. A. Ramsay, Astrophys. J. **137**, 89 (1963).

On the basis of these estimations, it may be seen that at 1470\AA formation of C_2 in the excited $\text{A}^3\Pi_g$ state is energetically impossible (even in zero vibrational level) and, hence, production of any of the Swan bands in emission is not to be expected in the photolysis of acetylene at this wavelength. Production of C_2 in the $\text{x}^1\Sigma_g^+$ ground state (or in the low-lying $\text{X}^3\Pi_u$ state) and molecular hydrogen is, however, energetically possible at this wavelength. At 1295\AA and at shorter wavelengths, formation of C_2 in the excited $\text{A}^3\Pi_g$ state is energetically possible (even to second vibrational level) and thus production of the Swan bands in emission is to be expected in the photolysis of acetylene at 1295\AA (Xe) and at 1236\AA and 1165\AA (Kr). These expectations exactly parallel our observations of hydrogen production at all wavelengths and observation of an emission only for wavelength 1295\AA and lower.

Using 52 kcal/mole for the heat of formation of a hydrogen atom, ΔH for the reaction



is estimated to be 249 kcal/mole. This reaction is therefore energetically impossible at even the shortest wavelength employed (1165\AA , 245 kcal/einstein) and need not be further considered.

The formation of $\text{C}_2(\text{A}^3\Pi_g)$ by



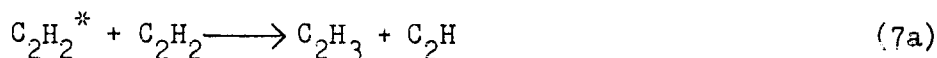
must be considered as an alternate means for producing excited C_2 and molecular hydrogen. This sequence could be distinguished from Reactions 5

or 6 by examining the isotopic distribution of the hydrogen produced in the photolysis of $C_2H_2-C_2D_2$ mixture. In Reactions 5 or 6, only H_2 and D_2 are formed whereas the above sequence should lead to both CH and CD, and hence H_2 , HD, and D_2 . Since it has not been possible here to obtain meaningful data from the photolysis of $C_2H_2-C_2D_2$ mixtures, distinction between the two processes cannot be made in this way. The absence of any evidence for participation of the CH radical in either vapor or solid-phase photolysis argues against the occurrence of Reactions 6b and 6c.

Since $\phi_{-C_2D_2} = 0.2$ and $\phi_{D_2} = 0.1$ in the 50 μ pressure region, the occurrence of other primary events of comparable importance to the formation of C_2 and molecular hydrogen is suggested. Our experiments present no evidence for or against the occurrence of Reaction 7:



However, both C_2H and C_2H_3 have been detected¹⁵ by ESR in the photolysis of acetylene at 1236 μ during deposition at 4°K from the gas phase. The formation of both radicals is completely suppressed when deposited acetylene is photolyzed and the authors suggested that the radicals were formed via an excited molecule reaction



which was suppressed in the solid phase. However, Reaction 7 followed by Reaction 8



15. E. L. Cochran, V. A. Bowers and F. J. Adrian, Sixth International Symposium on Free Radicals, Cambridge, England, July 1963.

appears to be an equally acceptable source of these radicals in the gas phase. If the hydrogen atom and ethynyl radical formed in Reaction 7 are not stabilized and if cage recombination occurs readily in the solid, appreciable concentrations of ethynyl and vinyl radicals will not be formed. It is of interest to note in this connection that the process leading to C_2 and molecular hydrogen still occurs to some extent in solid acetylene at $-196^\circ C$, since we have observed production of D_2 from solid C_2D_2 at $-196^\circ C$ and photolysis of trapped acetylene results in the observation of C_2 in absorption.¹⁶ Cage recombination of C_2 and H_2 would, of course, not be expected to be as likely to occur as recombination of H and C_2H , and our results are consistent with this expectation.

Reactions of Electronically Excited Acetylene

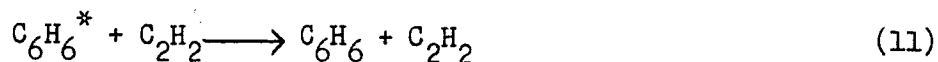
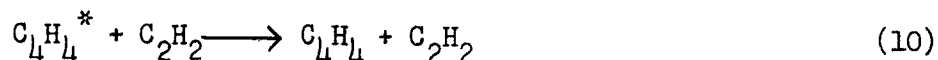
The observed polymer formation probably results from the occurrence of Reactions 3, 9, and similar reactions



since we have shown that with an increase in acetylene pressure from 56 μ to 2.4 mm Hg, polymer formation increases considerably and the quantum yield for disappearance of acetylene increases by a factor of 5 (Table 1-2). In the direct photolysis of acetylene at 1849\AA , the quantum yield for acetylene disappearance increased from two to 15 in the pressure region 1.8 to 47 mm Hg and a similar explanation involving an excited state of acetylene has

16. R. P. Frosh and G. W. Robinson, unpublished (quoted by G.W. Robinson in Free Radicals in Inorganic Chemistry, American Chemical Society, Washington, D.C., 1962.

been suggested. Collisional stabilization of the excited dimer and trimer



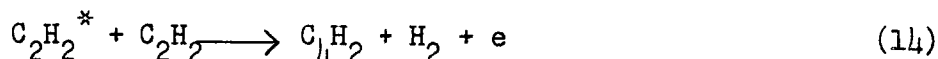
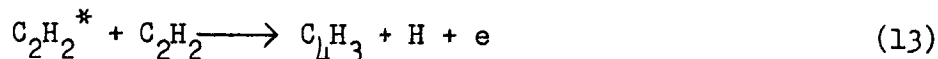
results in formation of vinyl acetylene and benzene.⁴ The diacetylene observed in photolysis⁴ probably results from recombination of ethynyl radicals



formed in Reaction 7. The presence of vinyl radicals¹⁵ in the system leads one to expect recombination to butadiene to occur. This has not been observed as a product in the photolysis of acetylene¹⁴ and a satisfactory explanation of these facts has yet to be given.

Koyano, Tanaka, and Omura¹⁷ have presented evidence for occurrence of chemi-ionization when acetylene vapor was photolyzed at 1216⁸Å.

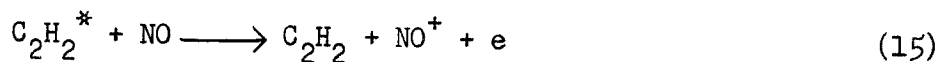
Their proposed reactions



followed by neutralization of the dimeric ions could also contribute to the increase in quantum yield for acetylene disappearance observed when the pressure of acetylene is increased. Reaction between excited acetylene and ground-state acetylene may also result in formation of ethynyl and vinyl radicals according to suggestion of Cochran, Bowers and Adrian.¹⁵

17. I. Koyano, I. Tanaka and I. Omura, J. Chem. Phys. 40, 2734 (1964).

Since Φ_{D_2} is reduced from 0.10 to 0.006 in the presence of 2 mm CO_2 and $\Phi_{-C_2D_2}$ is reduced from 0.20 to 0.01 in the presence of 2 mm N_2 , (Table 1-3) we may conclude that in the presence of these gases, the excited state of acetylene loses its energy by collision and does not decompose to form D_2 (Reaction 5 or 6) or, in fact, does not decompose appreciably at all. The reduction of the quantum yield for hydrogen production from 0.1 to 0.006 upon addition to $56 \mu NO$ to $56 \mu C_2D_2$ (Table 1-3) cannot be attributed to hydrogen-atom scavenging since acetylene itself is an efficient scavenger for hydrogen atoms. Since, under these conditions, 10% of light is absorbed by acetylene and 6% by the additional NO , the amount of light absorbed by acetylene is not sufficiently reduced by the presence of NO to explain the reduced hydrogen production. The most reasonable interpretation is, therefore, that the excited state of acetylene experiences collisional transfer of energy to nitric oxide resulting in decreased decomposition and, hence, decreased production of hydrogen. It is of interest to note in this regard that Tanaka¹⁸ has shown that excited acetylene can sensitize the ionization of NO .

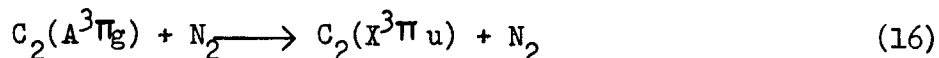


Quenching of the Emission

The $C_2(A^3\Pi_g)$ formed in decomposition of $C_2H_2^*$ may convert to the lower $X^3\Pi_u$ state by a radiative process (Reaction 5a) resulting in

18. I. Tanaka, Photochemistry Conference, Davis, California, June 1964.

emission of the Swan bands. Collisional quenching by N_2 (Reaction 16) is quite unlikely since



the radiative lifetime¹⁹ of C_2 in the $A^3\Pi_g$ state (1.4×10^{-7} sec) is too short for collisional deactivation and since the first excited triplet state of N_2 lies 6.5 eV above ground. The lifetime of $C_2H_2^*$ is, however, long enough for it to suffer collisions with walls or even with other molecules at low pressures. It is evident that the effect of added nitrogen will be primarily to deactivate the electronically excited acetylene



rather than deactivate $C_2(A^3\Pi_g)$.

Also, since at 2 mm N_2 , where the emission has been reduced almost to its minimum level (Figure 1-3), the quantum yield for disappearance of acetylene has been reduced from 0.20 to 0.01, the quenching of the emission is to be mainly attributed to the occurrence of Reaction 2a.

Acknowledgement

The authors are grateful to Dr. J. R. McNesby for his advice and comments throughout the course of the investigation.

19. W. S. Benedict and E. K. Plyler, National Bureau of Standards Circular 523, p. 54 (1954).

SECTION 2

ORIGIN OF THE $C_2(A^3\Pi_g) \longrightarrow C_2(X^3\Pi_u)$ EMISSION IN COMETS

2. Origin of the $C_2(A^3\Pi_g) \longrightarrow C_2(X^3\Pi_u)$ Emission in Comets

L. J. Stief and V. J. DeCarlo

The observation of the C_2 Swan bands ($A^3\Pi_g \longrightarrow X^3\Pi_u$) in emission in the coma of comets was at one time taken as evidence that the ground state of C_2 was the $X^3\Pi_u$ state since this cometary emission is known to arise via a fluorescence process. However, Ballik and Ramsay¹ have shown that the ground state of C_2 is $X^1\Sigma_g^+$ and consequently the observation of the Swan bands would be consistent with the following:

(1) C_2 is formed initially in the triplet system by decomposition (probably photodecomposition) of a hydrocarbon molecule.

(2) The $^3\Pi_u \longrightarrow ^1\Sigma_g^+$ transition does not occur to an appreciable extent prior to fluorescence excitation by solar radiation or in the time between successive excitations.

The latter implies that C_2 experiences an insufficient number of collisions, or possibly no collisions, to effect the forbidden $^3\Pi_u \longrightarrow ^1\Sigma_g^+$ transition. This is not an unreasonable requirement since it is known that the rotational and vibrational distribution of C_2 in cometary atmosphere corresponds to a temperature of about 2500°K and that C_2 , therefore, must experience few if any collisions between the time of its formation near the nucleus and the time of its excitation farther out in the coma.

Thus, while the second requirement seems to be met, the first requirement of the specific formation of C_2 in the triplet system upon photodissociation of a hydrocarbon molecule needs to be demonstrated. Any significant formation of C_2 in the singlet system must be excluded since appreciable concentrations

1. E. A. Ballik and D. A. Ramsay, J. Chem. Phys. **31**, 1138 (1959).

Note: This Section has been published under the above title in Nature, **205**, 1197 (1965)

of C_2 in the $x^1\Sigma_g^+$ ground state would eventually lead to population of upper singlet states ($b^1\Pi_u$, $c^1\Pi_g$, $d^1\Sigma_u^+$) and emission from these states. (See Figure 2-1.)

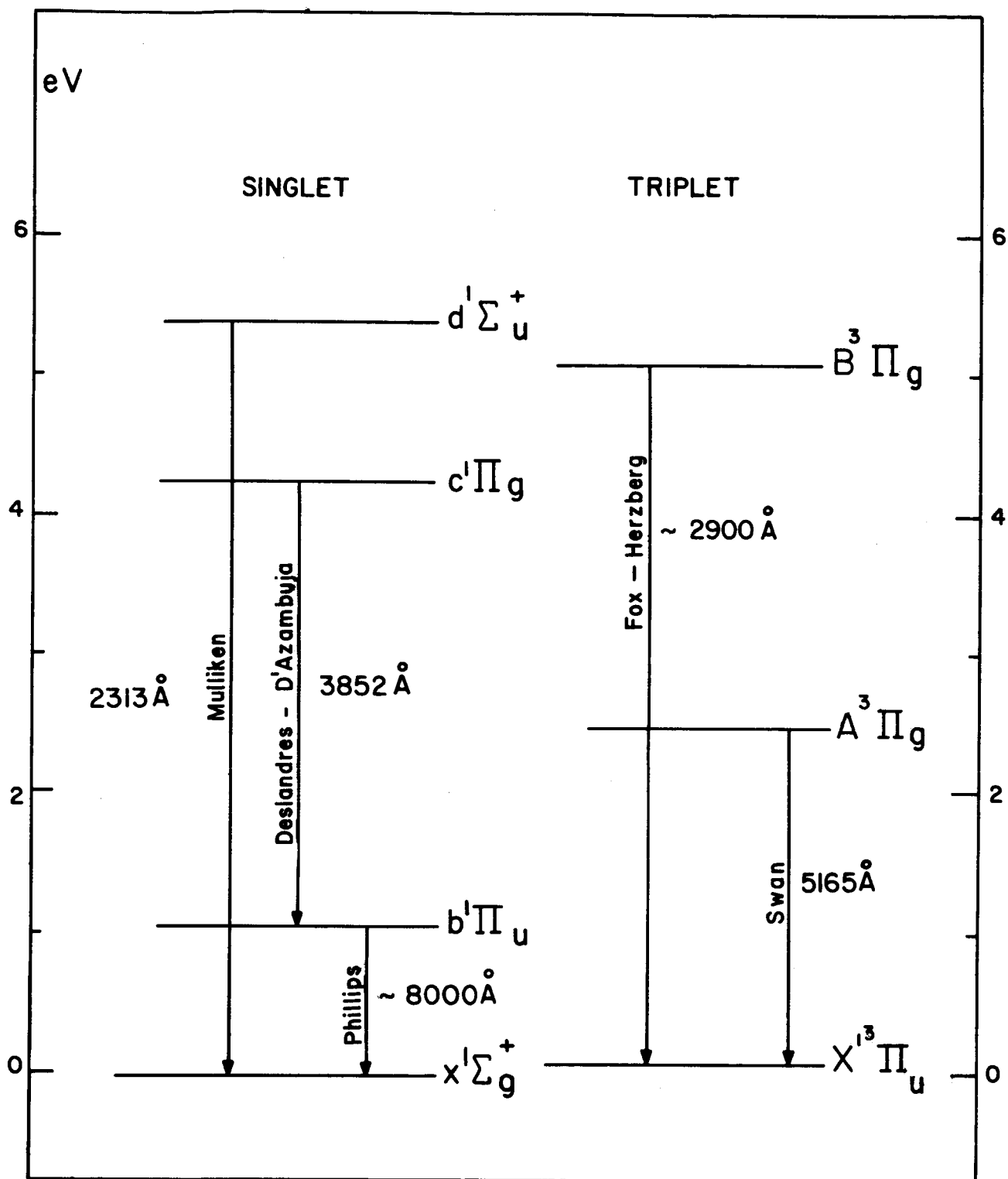
Recent work in our laboratory on the vacuum ultraviolet photolysis of CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 suggests that photodissociation of methane and acetylene in the vacuum ultraviolet at low pressures leads to the formation of C_2 in the $3\Pi_g$ state. The emission from CH_4 was very weak and since a secondary process for C_2 production from methane is required, the more interesting C_2H_2 system was studied in detail. A weak emission consistent with the Swan bands of C_2 and the detection of molecular hydrogen formation was explained in terms of the decomposition of an electronically excited acetylene molecule.²



Emission in the regions of other C_2 transitions (see Figure 2-1) was not observed. No emissions were observed from C_2H_4 and C_2H_6 .

On this basis we would suggest that the origin of the C_2 Swan bands in cometary emission spectra is the photodissociation of acetylene or an acetylene-type molecule leading to an eventual accumulation of C_2 in the $X^3\Pi_u$ state.

2. L. J. Stief, V. J. DeCarlo and R. J. Mataloni, J. Chem. Phys. (1965) in press.

Figure 2-1. Energy Level Diagram of C_2

SECTION 3

VACUUM ULTRAVIOLET PHOTOLYSIS OF HYDRAZINE

3. Vacuum Ultraviolet Photochemistry. III. Photolysis of Hydrazine

L. J. Stief, V. J. DeCarlo and R. J. Mataloni

3.1 Introduction

Photochemical studies of simple nitrogen-hydrogen compounds have been mainly concerned with understanding the decomposition of ammonia, and a recent review by McNesby and Okabe¹ discusses the primary and secondary processes determined for this system. Limited work is available on the photochemical decomposition of hydrazine. This includes the earlier kinetic studies of Elgin and Taylor,² and Wenner and Beckman³ at wavelengths above 1900Å. Spectroscopic studies have been reported by Ramsay⁴ on the flash photolysis of N₂H₄, and the NH emission produced by vacuum ultraviolet photolysis of N₂H₄ has recently been reported by Becker and Welge.⁵

The present study is a continuation of work investigating potential primary photochemical processes occurring in simple molecules. In these studies low pressures, emission spectra, and product analysis are used to develop reaction mechanisms.

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1. J. R. McNesby and H. Okabe, "Vacuum Ultraviolet Photochemistry," Advances in Photochemistry, Volume 3, Interscience Publishers, New York, 1964.
 2. J. C. Elgin and H. S. Taylor, J. Am. Chem. Soc. 51, 2059 (1929).
 3. R. P. Wenner and A. O. Beckman, J. Am. Chem. Soc. 54, 2787 (1932).
 4. D. A. Ramsay, J. Phys. Chem. 57, 415 (1953).
 5. K. H. Becker and K. H. Welge, Z. Naturforsch 19a, 1006 (1964).

NOTE: This work will be submitted for publication at a later date.

3.2 Experimental

Light Sources and Actinometry

The xenon and krypton resonance lamps were excited in an air-cooled electrodeless discharge operated by a Raytheon 2450-MC microwave generator. The krypton lamp was filled with 1 mm Hg of pure gas and cooled with liquid nitrogen; the xenon lamp was filled with 750 μ Hg of pure gas and cooled with liquid oxygen. The krypton resonance lamp, emitting radiation at 1236\AA (10 eV) and 1165\AA (10.6 eV) was fitted with a CaF window to remove the 1165\AA line. This window reduces the intensity of the 1236\AA line by one third. The xenon resonance lamp, emitting radiation at 1470\AA (8.4 eV) and at 1295\AA (9.6 eV) was constructed with a sapphire window which removed the 1295\AA line and did not appreciably affect the intensity of the 1470\AA line. The windows were attached to the lamps using "Torr Seal" from Varian Associates. The spectral purity of the krypton lamp was checked by attempting to photolyze CO_2 or N_2H_4 in a cell fitted with a sapphire window; the purity of the xenon lamp was tested by using an ethane gas filter which absorbed 99% of the radiation at 1550\AA but transmitted 80% at 1600\AA . No photodecomposition of CO_2 or N_2H_4 was detected after a half-hour photolysis, thus indicating that no impurity lines were present above the transmission level of the filters. Previous measurements of the emission spectra of these lamps showed that impurity lines, when present, were always above 1600\AA . Lamp intensities were obtained by CO_2 actinometry, and were usually between 10^{15} and 10^{16} quanta/second.

The hydrogen discharge lamp used in these studies was Model 471A-32 obtained from Hanovia Lamp Division, Newark, New Jersey. The lamp had a sapphire window and was operated at 2000 volts and 450 milliamperes.

Materials

Technical-grade hydrazine was obtained from Olin Matheson Chemical Corp., New York, New York. Spectroscopic analysis of the sample indicated severe contamination with ammonia and water. The ammonia was removed by several distillations in vacuo from a trap at -78° to one at -196°C . Water could not be removed in this manner since the melting points of water and hydrazine are quite similar. The hydrazine was dried by passing it through a tube filled with anhydrous calcium sulfate. The effectiveness of removal of NH_3 and H_2O from the hydrazine was monitored by observing the level of the 3240\AA NH emission and the 3064\AA OH emission, respectively, when the sample was exposed to krypton resonance radiation. Since for comparable pressures of H_2O and N_2H_4 , the OH emission is at least 10^3 times more intense than the NH emission, the final level of water impurity is probably below 0.01%. Many passes over the calcium sulfate drying agent were required to bring the water impurity to this level. The hydrazine sample was stored at -78°C .

Krypton and xenon were obtained from the Air Reduction Company, Jersey City, New Jersey. The known impurities were 150 ppm Xe in krypton and less than 20 ppm Kr in xenon. Research-grade nitrogen, hydrogen, and carbon dioxide were obtained from the Matheson Co., Inc., East Rutherford, New Jersey. Ethylene- d_4 was obtained from Merck and Co., Montreal, Canada.

Procedure

Two mercury-free Pyrex reaction cells were used. One reaction cell had a volume of 458 cc and an absorption path of approximately 15 cm and was fitted with a 25 mm diameter LiF entrance window at right angles to a 25 mm diameter quartz exit window. The other reaction cell had a volume of 2069 cc and an absorption path of approximately 28 cm and was fitted with a 25 mm diameter LiF entrance window at right angles to a 25 mm diameter sapphire exit window. Windows were sealed to the reaction cells with "Torr Seal". Two horn-shaped light traps were incorporated into the cells, one directly opposite each window. The cells were sprayed with 3M Velvet Coating paint to form a light-tight system.

The vacuum system was also mercury free and stopcocks were greased with Apiezon-N grease. Pressures were measured in the reaction volume with a Granville Phillips capacitance manometer which was used as a direct reading instrument. The capacitance manometer was calibrated against the vapor pressure of several materials at three to four different temperatures each.

The window of the light source rested against the entrance window of the reaction cell. It was found that little or no resonance radiation was absorbed in the small air gap between the two windows. The entrance slit of an f/3.5 Bausch & Lomb monochromator ($32\text{\AA}/\text{mm}$ dispersion between 2000 and 4000\AA and $64\text{\AA}/\text{mm}$ dispersion between 3500 and 8000\AA) was placed at the exit window of the cell with a 1P28 (S-5 response) or 1P21 (S-4 response) phototube operated from an Aminco microphotometer at the exit slit of the monochromator. The monochromator was modified into a recording instrument and the emissions were recorded on an E.A.I. Model 1110 Variplotter.

In those experiments where product formation and disappearance of hydrazine were studied, the pressure of nitrogen and hydrogen was measured at -196°C , since these were the only products not condensable at this temperature. The sample was then expanded into a sample bulb of a volume which was approximately equal to the mean between the volume of the reaction cell and the expansion volume of the CEC 21-130 mass spectrometer. The remainder of the sample was pumped away and the pressure of ammonia was measured with the trap at -78°C . Hydrazine pressure was measured at the beginning and at the end of each experiment.

The sensitivity of the spectrometer to nitrogen and hydrogen was found to vary with pressure. To compensate for this, a standard mixture of nitrogen and hydrogen was run at a series of pressures. The sensitivity was calculated for each pressure and a correction plot was made of sensitivity versus pressure. Mass spectrometer analysis was not carried out on ammonia or hydrazine, since both hydrazine and ammonia adsorbed very strongly on the walls of the instrument.

3.3 Results

Spectroscopic Observations

When pure hydrazine is photolyzed with the krypton resonance lines, an emission was observed at 3360\AA . Except for the small OH emission produced from the trace concentration of water, no other emissions were noted in the range 2000\AA to 7000\AA . The spectrum obtained at 25°C and 50 u Hg pressure is shown in Figure 3-1a. The entire spectrum has been recorded for the pressure range 10 u to 2 mm Hg. The maximum emission occurs at 50 u Hg (Figure 3-2) with definite decrease in intensity for both higher and lower pressures of hydrazine.

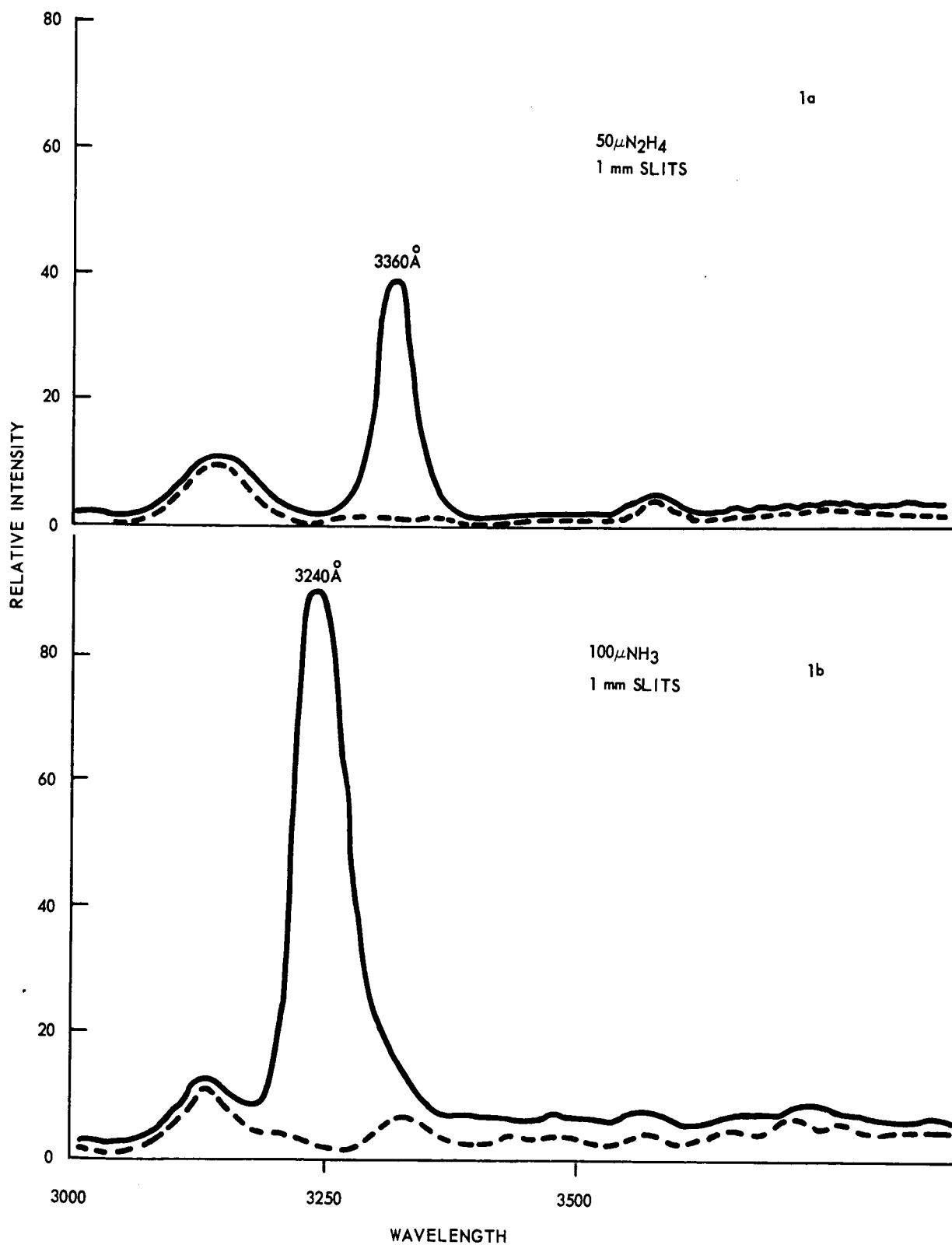


Figure 3-1. (a) Emission Spectrum Observed During Photolysis of Hydrazine at 50μ Hg Pressure and 1236 Å

(b) Emission Spectrum Observed During Photolysis of Ammonia at 100μ Hg Pressure and 1236 Å

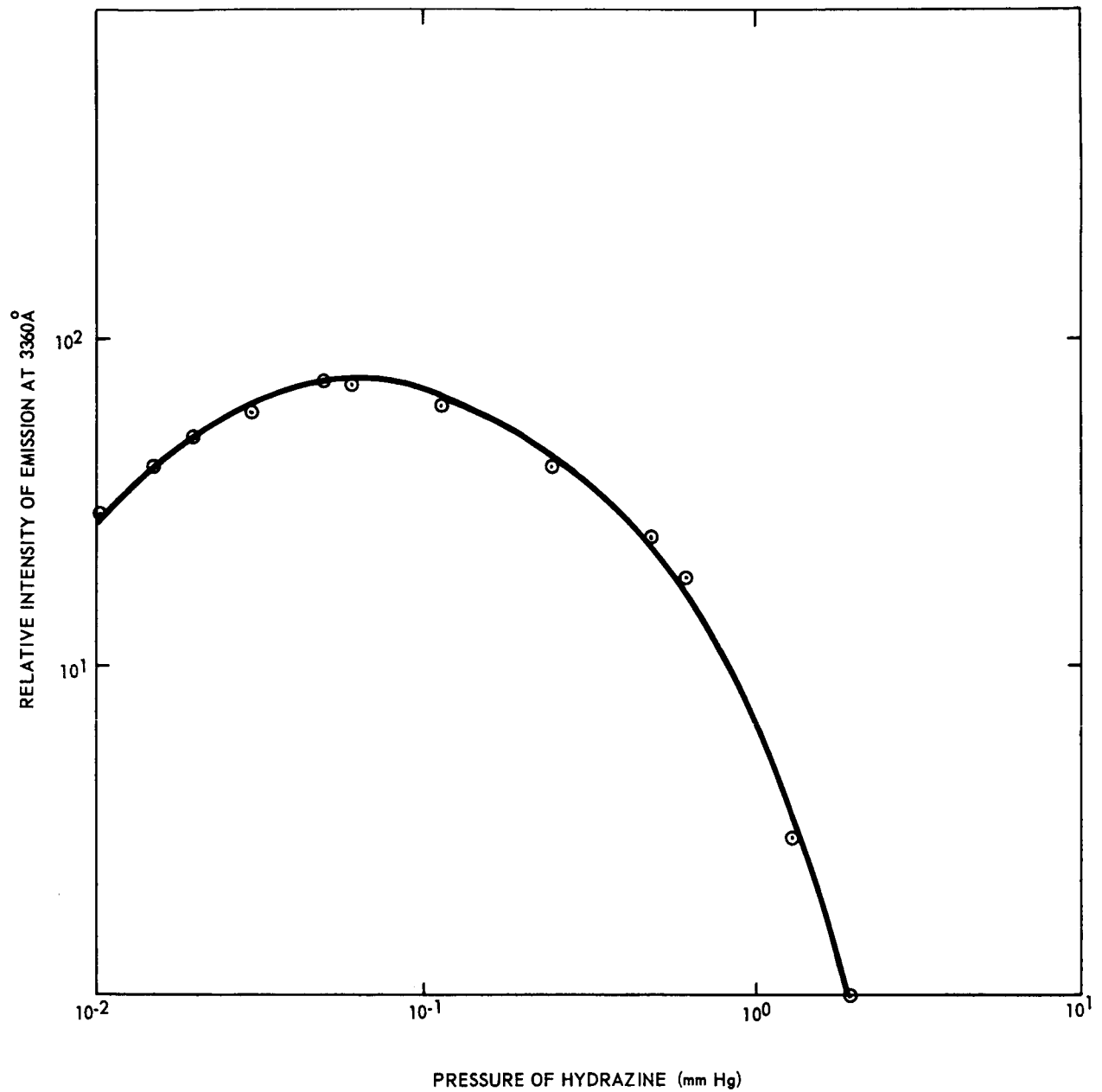


Figure 3-2. Effect of Hydrazine Pressure on Intensity of Emission at 3360 Å
Observed During Photolysis of Hydrazine at 1236 Å

The effect of the addition of nitrogen, along with the effect of additional hydrazine, on the intensity of emission is shown in Figure 3-3. It can be seen from Figure 3-3 that the addition of small amounts of hydrazine quickly reduces the intensity of emission whereas the addition of nitrogen, even up to a few millimeters, has very little effect on the intensity.

By continuously monitoring the region 3000\AA to 3500\AA during hydrazine photolysis, an increase in the intensity of emission at 3240\AA and a concurrent decrease in the emission at 3360\AA is noted as shown in Figure 3-4. These results confirm the observations of Becker and Welge⁵ on the effect of pressure and duration of the photolysis on the observed emissions. The gradual decrease in the intensity of emission at 3360\AA and increase at 3240\AA may be attributed to increased absorption of the light by the ammonia being formed as a product of hydrazine photolysis, which is then subsequently photolyzed to give the emission at 3240\AA . To test this, a sample of hydrazine was photolyzed at 1236\AA until the emission at 3240\AA was equal to that at 3360\AA . The trap on the photolysis cell was then cooled to -78°C which condensed the hydrazine but did not affect the ammonia since ammonia has a vapor pressure of 30 mm at -78°C . The emission at 3360\AA disappeared but there was no effect on the emission at 3240\AA . The trap was then further cooled to -196°C which removed the 3240\AA emission. When the sample was warmed to room temperature both emissions at 3240\AA and 3360\AA reappeared. In addition to this experiment a pure sample of ammonia at 25°C and 100 u Hg was photolyzed with the krypton lamp and an emission was noted at 3240\AA as is shown in Figure 3-1b.

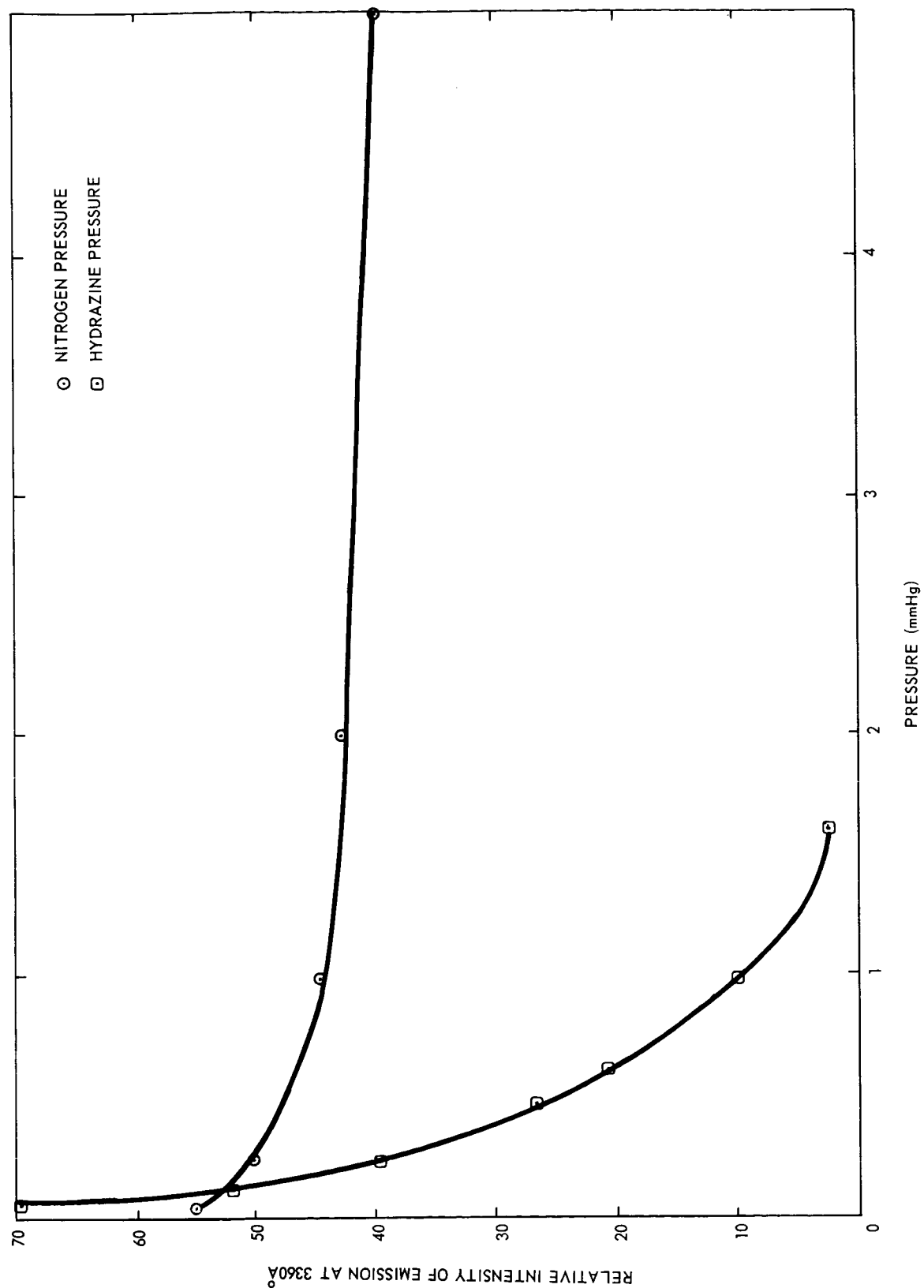


Figure 3-3. Effect of Nitrogen (○) and Hydrazine (□) on the Intensity of Emission Observed During the Photolysis of Hydrazine at 1236 Å

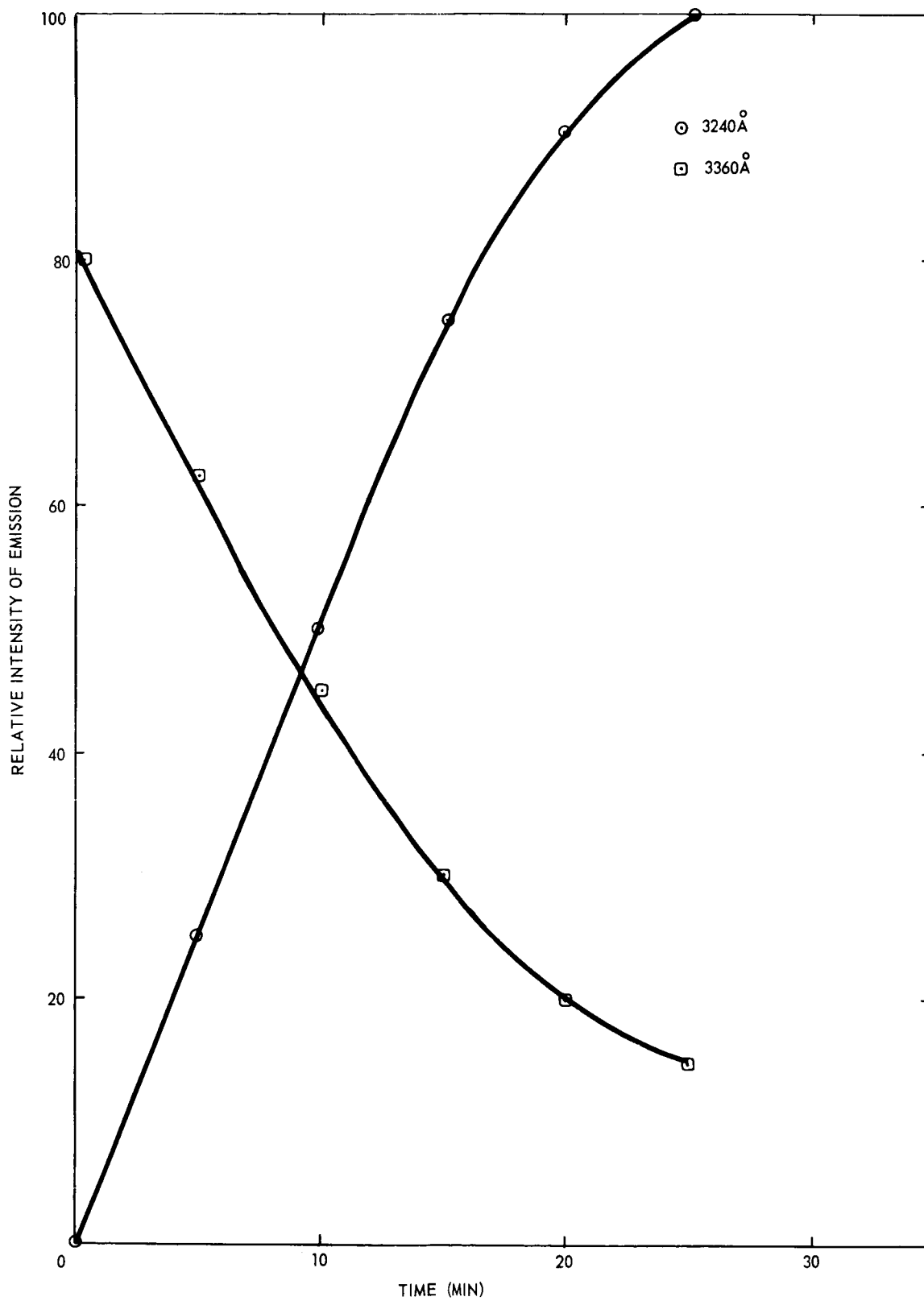


Figure 3-4. Increase in Intensity of Emission Observed at 3240 Å (⊙) and Decrease in Intensity at 3360 Å (⊠) During Prolonged Photolysis of Hydrazine at 50 μ Hg Pressures and 1236 Å

No other emissions were noted in the region 2000\AA to 3500\AA . A strong continuum in the region 4000\AA to 5500\AA was noted when the lamps were used with a relatively fresh LiF window. After the lamps had been in use for a few hours, the emission was quite weak and indistinguishable from the background.

A pure sample of hydrazine was photolyzed with the krypton resonance lines and the amount of ammonia produced together with the amount of hydrazine destroyed was recorded as a function of time. The percentage of light absorbed by the ammonia and hydrazine was calculated. A plot of absorbed light versus time is shown in Figure 3-5. It is significant to note that the time of equal light absorption by the ammonia and hydrazine corresponds to the time at which the emissions are of equal intensity.

When a sample of hydrazine was photolyzed with the xenon resonance lines, no emissions were noted in the region 2000\AA to 7000\AA . A very weak emission at 3360\AA was observed when the hydrogen discharge lamp was used for photolysis. Ammonia photolysis with the hydrogen discharge lamp did not produce the NH_2 bands observed by Neumin and Terenin.⁶

Product Formation

Photolysis at 1236\AA - The products determined in the photolysis of hydrazine are hydrogen, nitrogen, and ammonia. The pressure dependence of quantum yield for product formation and for hydrazine disappearance have been determined at the krypton and xenon resonance lines. The CO_2 used for actinometry was photolyzed in the emission cell, with intensity

6. H. Neumin and A. Terenin, Acta Physicochim URSS, 5, 465 (1936).

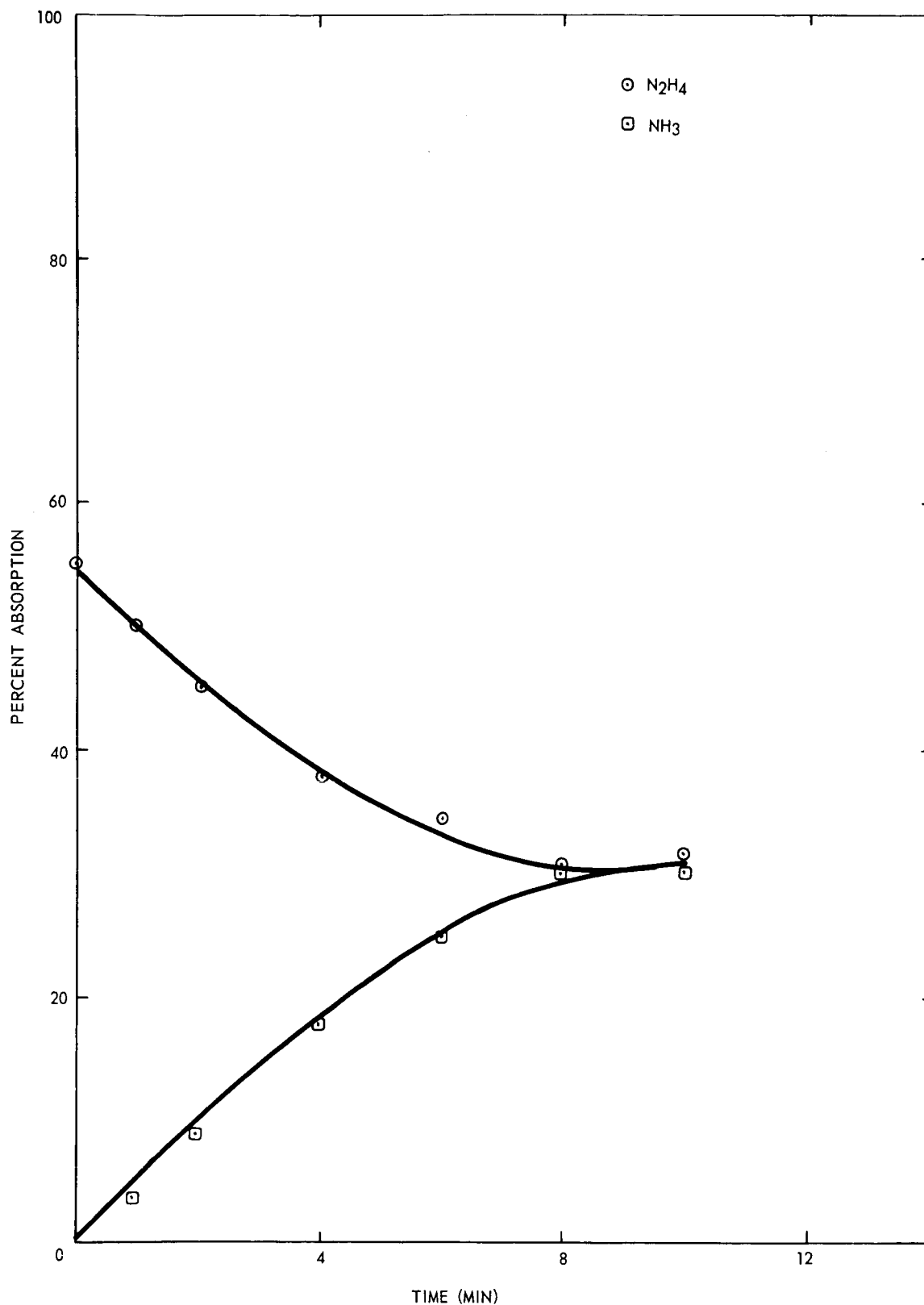


Figure 3-5. Percent of 1236 Å Radiation Absorbed by Hydrazine (○) and Ammonia (□) During Prolonged Photolysis of Hydrazine at 100 μ Hg Pressure and 1236 Å

measurements being made at regular intervals. The production of CO from CO₂ photolysis at 10 mm is linear with time up to at least 30 minutes.

The effect of hydrazine pressure on the quantum yield for the formation of hydrogen, nitrogen, and ammonia as well as for hydrazine disappearance from hydrazine photolysis at 1236⁰Å is shown in Figure 3-6 and tabulated in Table 3-1. The quantum yields were measured at 100 u, 1 mm, 2 mm, and 3 mm Hg and were found to be independent of time up to at least ten minutes. The quantum yields were found to increase with pressure. The quantum yield for nitrogen and ammonia is quite reproducible and appears to be linear with pressure. The quantum yield for hydrogen production is erratic but does seem to tend toward linearity. There is probably a contribution to the hydrogen production from the presence of water in the hydrazine sample and/or on the walls of the vacuum system. The quantum yield for disappearance of hydrazine is shown to increase rapidly with pressure reaching a value of 8 at 2 mm Hg. Quantum yields for hydrazine disappearance at the high pressures are not as accurate as those at low pressures because of the scale sensitivity of the manometer at higher pressures and because the relative change in hydrazine pressure is small.

Photolysis at 1470⁰Å - The effect of hydrazine pressure on the quantum yield for the formation of hydrogen, nitrogen, and ammonia as well as hydrazine disappearance from hydrazine photolysis at 1470⁰Å is shown in Figure 3-7 and tabulated in Table 3-2. The quantum yields were observed at 100 u, 150 u, 500 u, and 1 mm Hg and were found to be independent of time up to at least 12 minutes. Product formation as a function of time

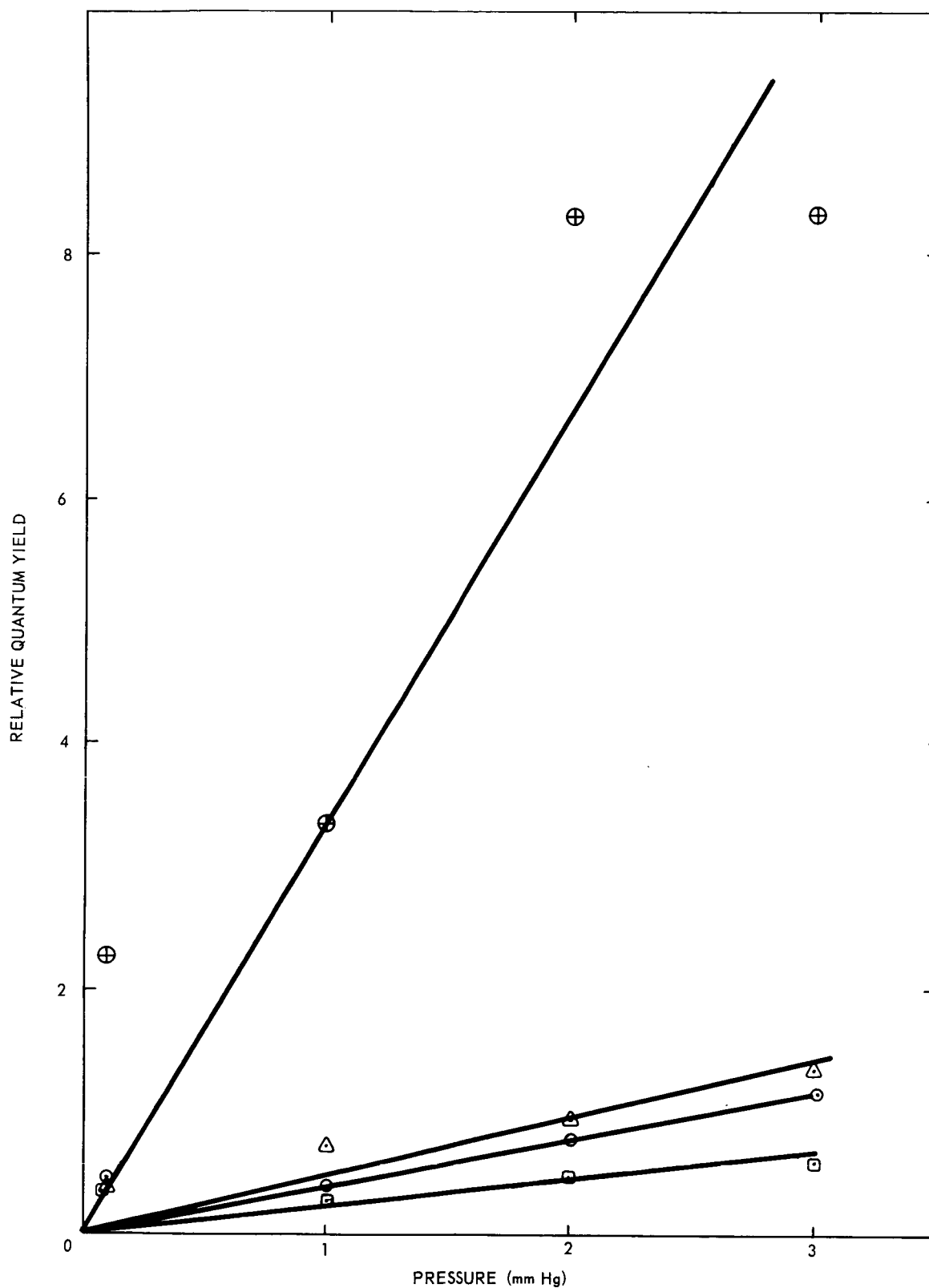


Figure 3-6. Pressure Dependence of Relative Quantum Yield for Hydrogen (⊙), Nitrogen (⊠), Ammonia (Δ) and Hydrazine Disappearance (⊕) in the Photolysis of Hydrazine at (1165 Å and 1236 Å).

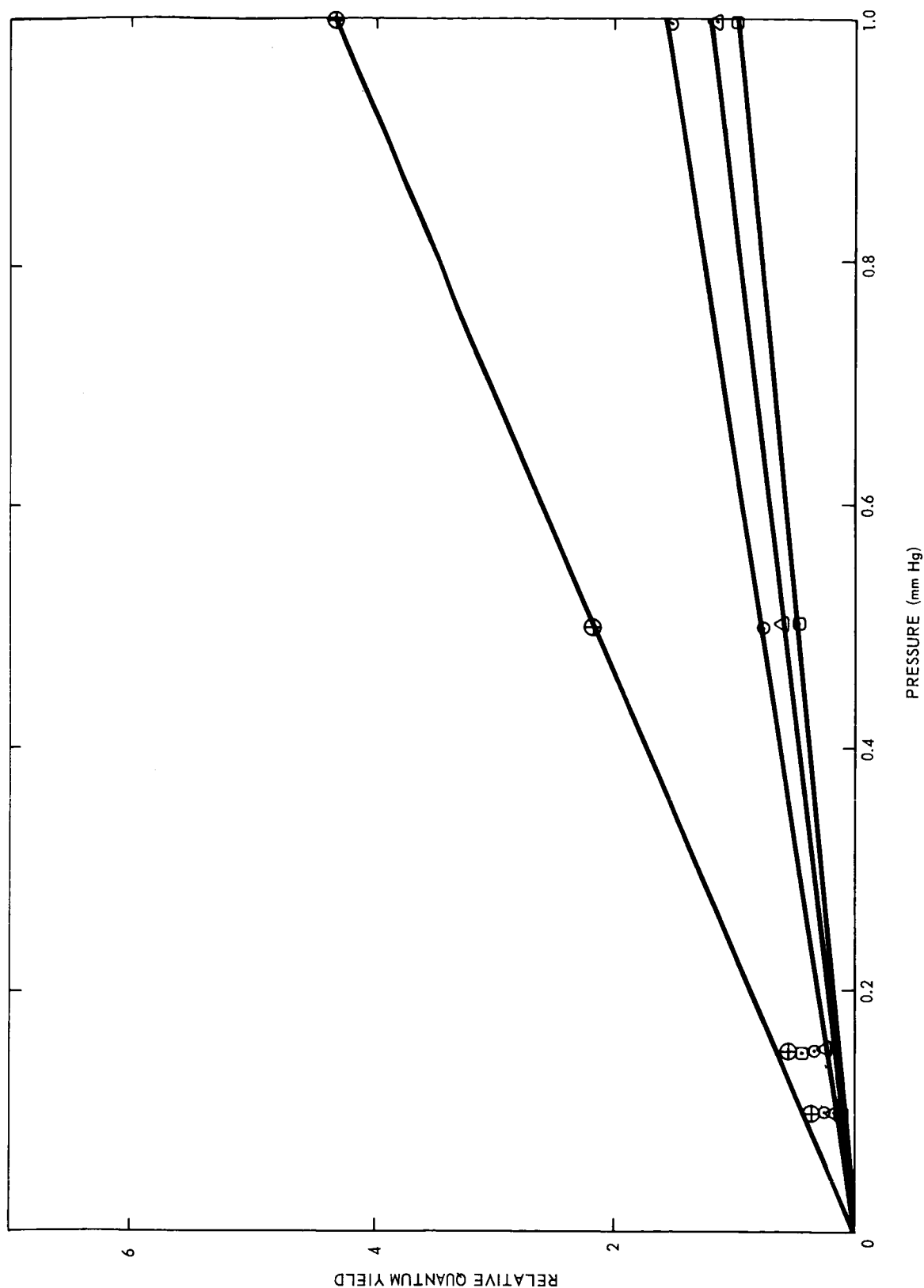


Figure 3-7. Pressure Dependence of Relative Quantum Yield for Hydrogen (●), Nitrogen (◻), Ammonia (Δ), and Hydrazine Disappearance (⊕) in the Photolysis of Hydrazine at 1470 Å

Table 3-1

Effect of Pressure on the Quantum Yield (Φ) of Product Formation
and Hydrazine Disappearance in the Photolysis of Hydrazine
at the Krypton Resonance Line (1236Å)

	Pressure of Hydrazine			
	100 u	1mm	2mm	3mm
% absorption	53	100	100	100
Φ_{H_2}	0.48 ± 0.14	0.90	0.77	1.11 ± 0.06
Φ_{N_2}	0.37 ± 0.12	0.43	0.51	0.53 ± 0.07
Φ_{NH_3}	0.40 ± 0.08	0.91	0.95	1.14 ± 0.02
$\Phi_{-N_2H_4}$	2.26 ± 1.39	3.32	8.30	8.30

Table 3-2

Effect of Pressure on the Quantum Yield (Φ) of Product Formation
and Hydrazine Disappearance in the Photolysis of Hydrazine
at the Xenon Resonance Line (1470Å)

	Pressure of Hydrazine			
	100 u	150 u	500 u	1mm
% absorption	35	48	89	100
Φ_{H_2}	0.37	0.58 ± 0.02	0.72 ± 0.07	1.50 ± 0.28
Φ_{N_2}	0.27	0.48 ± 0.01	0.45 ± 0.01	0.95 ± 0.27
Φ_{NH_3}	0.21	0.32 ± 0.03	0.44 ± 0.04	1.16 ± 0.21
$\Phi_{-N_2H_4}$	0.21	0.61 ± 0.12	2.19 ± 0.16	4.30 ± 1.70

at 100 u Hg for 1470\AA is shown in Figure 3-8. The time and pressure dependence of product formation at lower pressures was found to be better behaved for photolysis at 1470\AA than at 1236\AA . The quantum yield for hydrogen, nitrogen, and ammonia was found to increase with pressure, while the quantum yield for hydrazine disappearance was found to increase rapidly with pressure.

The N/H ratio for the products found for the photolysis of N_2H_4 below 1 mm is 2 to 3.4. This is in the range where the quantum yield for hydrazine disappearance increases from 0.2 to 2.0 and indicates a slight deficiency in hydrogen. At 1 mm where the quantum yield for hydrazine disappearance is larger, the N/H ratio is 2 to 7 indicating a drastic loss of nitrogen-rich products. A true material balance is obtained only for the 150 u Hg experiments.

The effect of added gases on the production of ammonia from 150 u of hydrazine using 1470\AA is shown in Table 3-3. There is a definite increase in production of ammonia and hydrazine disappearance by the addition of 1 mm of nitrogen. There is a slight increase with the addition of 1 mm of hydrogen, but not quite as pronounced as the addition of nitrogen.

The effect of adding C_2D_4 as a scavenger for hydrogen atoms in the photolysis of 500 u of N_2H_4 with 1470\AA radiation is shown in Table 3-4. The quantum yield for hydrogen production and the quantum yield for hydrazine disappearance are both reduced by the addition of 5% or 20% C_2D_4 . There appears to be no affect on the quantum yield for nitrogen production with the addition of C_2D_4 . The values of the quantum yields were corrected for the percentage of resonance radiation absorbed by the C_2D_4 .

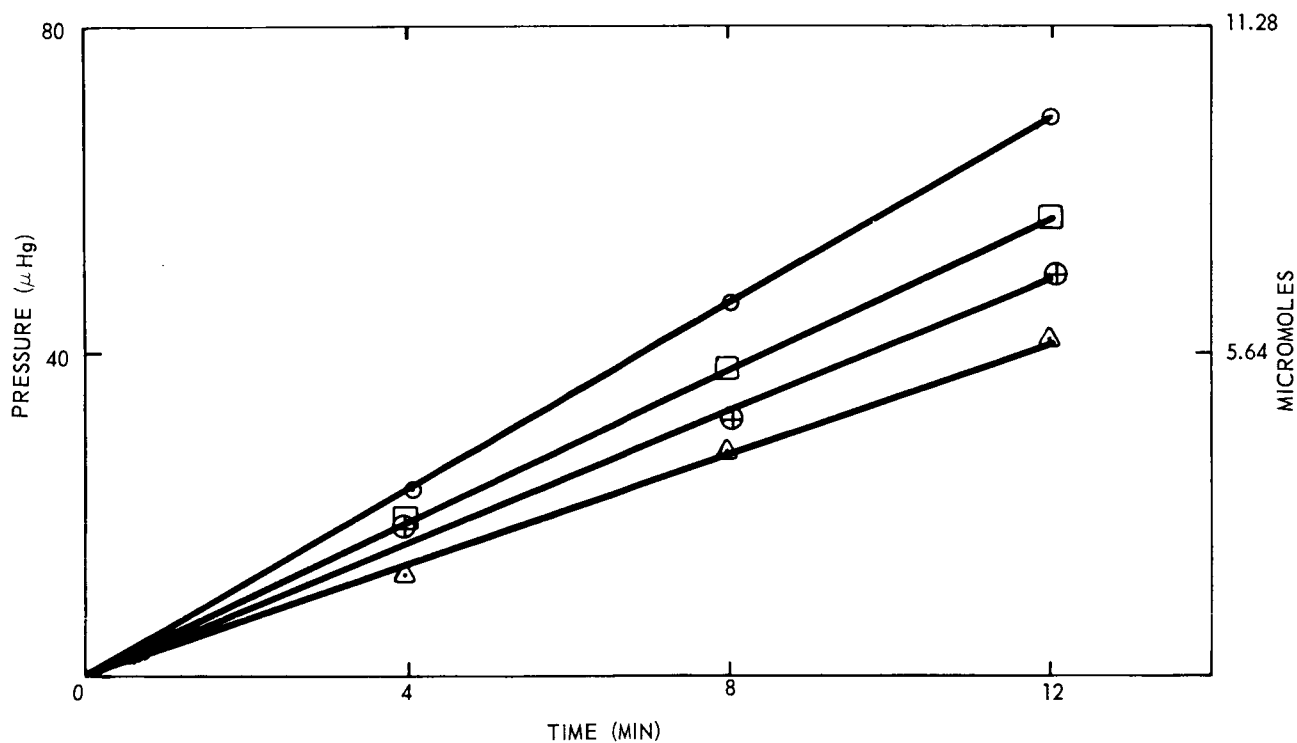


Figure 3-8. Time Dependence of Product Formation of Hydrogen (○), Nitrogen (◻), Ammonia (Δ), and Hydrazine Disappearance (⊕) in the Photolysis of Hydrazine at 100μ Hg Pressure and 1470\AA (⊕)

Table 3-3

Effect of Added Gases on Ammonia Production and Hydrazine
Disappearance in Photolysis of 150 u Hydrazine at 1470Å

Quantum Yield	Added Gas (1 mm Hg)		
	None	Nitrogen	Hydrogen
Φ_{NH_3}	0.32 ± 0.03	0.86 ± 0.06	0.56
$\Phi_{-\text{N}_2\text{H}_4}$	0.61 ± 0.12	2.73 ± 0.17	1.36

Table 3-4

Effect of Adding C_2D_4 on Hydrogen and Nitrogen Production and
Hydrazine Disappearance in Photolysis of 500 u
of Hydrazine at 1470Å

Quantum Yield	Pressure of Added C_2D_4		
	None	25 u Hg	100 u Hg
Φ_{H_2}	0.72	0.50	0.55
Φ_{N_2}	0.45	0.40	0.49
$\Phi_{-\text{N}_2\text{H}_4}$	2.19	1.59	1.60

All these results refer to experiments performed in the smaller (458 cc) cell with the shorter (15 cm) path length. It was found that experiments at the same pressure in the larger cell (2000 cc and 28 cm path length) lead to quantum yields twice that observed in the smaller cell, although the distribution of the products was not measurably altered. However, experiments at comparable absorbed intensities but different pressures in the two cells gave essentially the same quantum yields. Thus quantum yields show some dependence on intensity and/or

surface-to-volume ratio. These effects have not been systematically examined in these experiments. However, in one set of experiments where the pressure of hydrazine was kept constant while the intensity of radiation emitted by the lamp was increased, the rate of production of N_2 and H_2 increased much more rapidly than the rate of NH_3 production.

3.4 Discussion

Photolysis at 1236 \AA

Since the ionization potential of N_2H_4 is 9.0 eV,⁷ photolysis at 1236 \AA (10 eV) leads to substantial formation of the parent ion $N_2H_4^+$. The reactions of this ion have not been investigated. Isotopic labeling techniques, such as used in the study of the $C_3H_6^+$ ion produced by photoionization of C_3H_6 ,⁸ can not be employed here since the hydrogens in hydrazine are readily exchanged. Thus, little can be said at this time concerning the primary process leading to the emission observed and the products formed in the photolysis of hydrazine at the krypton resonance line.

If neutralization of the parent ion occurs to some extent



or if direct excitation occurs



without ionization (ionization efficiency less than 100%), the following

-
7. V. H. Dibeler, J. L. Franklin, and R. M. Reese, J. Am. Chem. Soc. **81**, 68 (1959).
 8. R. D. Doepker, R. Gordon, Jr., and P. Ausloos, Abstracts 149th National Meeting, American Chemical Society, Detroit, Michigan, April 1965.

Photolysis at 1470Å

Two complications present at 1236Å, namely ionization of N_2H_4 and subsequent photolysis of the ammonia product, do not occur at 1470Å. The absorption coefficients of N_2H_4 and NH_3 at 1470Å⁵ are such that absorption by ammonia may be neglected even for the lowest pressures of N_2H_4 employed. The relative importance of various primary processes cannot be evaluated from the present data.

The following reactions are energetically possible at 1470Å (194 kcal/einstein):

<u>Reaction</u>	<u>ΔH kcal/mole</u>	
$N_2H_4 \longrightarrow NH + NH_3^*$	49	(6)
$N_2H_4 \longrightarrow NH_2 + NH_2^*$	59	(7)
$N_2H_4 \longrightarrow H + N_2H_3^*$	94(?)	(8)
$N_2H_4 \longrightarrow NH + NH + H_2$	143	(9)
$N_2H_4 \longrightarrow NH + NH_2 + H$	153	(10)

The NH_3 , NH_2 , and N_2H_3 formed in Reactions (6), (7), and (8) respectively could contain considerable excess energy. The maximum amount would be the difference between the energy of the incident photon and the ΔH of the reaction leading to the species in question. If this excess energy is not removed by collision with other molecules, decomposition of the excited species may occur. Below are tabulated the possible decomposition reaction for these excited species, the maximum possible excitation energy in the excited species, and the ΔH for the decomposition reaction.

<u>Excitation Energy of the Excited Species (kcal/mole)</u>	<u>Decomposition Reaction</u>	<u>ΔH (kcal/mole)</u>	
145	$\text{NH}_3^* \longrightarrow \text{NH}_2 + \text{H}$	104	(11)
145	$\text{NH}_3^* \longrightarrow \text{NH} + \text{H}_2$	94	(12)
135	$\text{NH}_2^* \longrightarrow \text{NH} + \text{H}$	85	(13)
90	$\text{N}_2\text{H}_3^* \longrightarrow \text{NH}_2 + \text{NH}$	59(?)	(14)

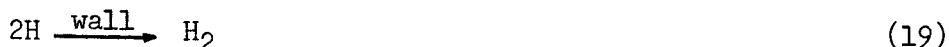
In all cases there is sufficient energy for the decomposition to occur. The sequence of Reactions (6), (7), or (8) followed by Reactions (11), (12), (13), or (14) is equivalent to the over-all Reactions (9) or (10).

The occurrence of Reaction (15)

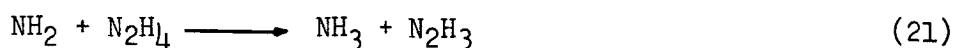
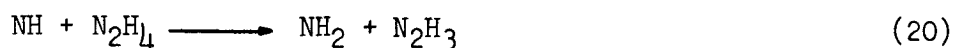


either directly or through the subsequent decomposition of an excited intermediate is energetically impossible at 1470Å.

The nitrogen, hydrogen, and ammonia observed as products of the photolysis of hydrazine at 1470Å may be formed by radical-radical reactions



by abstraction reactions



or possibly by direct molecular detachment [Reactions (6) and (9)].

disappearance observed at 100 and 150 u Hg pressure may be due to contribution from the reaction



Quenching of excited N_2H_4^* can not be the cause of the low quantum yields because increased pressure of N_2H_4 or addition of N_2 would then result in even lower values for the quantum yield for hydrazine disappearance. The opposite is actually observed and has been interpreted above in terms of quenching of NH_3^* , NH_2^* , and N_2H_3^* .

Acknowledgements

The authors wish to express their gratitude to Drs. James R. McNesby and Arnold M. Bass for their advice and consultation throughout the course of the investigation.

We also wish to thank Dr. K. H. Welge for stimulating discussions on hydrazine photolysis.

SECTION 4

ORIGIN OF $\text{NH}(\text{A}^3\Pi) \longrightarrow \text{NH}(\text{X}^3\Sigma^-)$ EMISSION IN COMETS

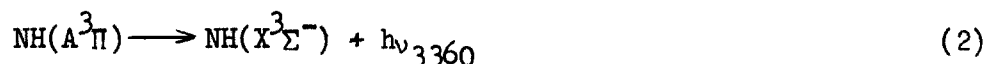
4. Origin of $\text{NH}(\text{A}^3\Pi) \rightarrow \text{NH}(\text{X}^3\Sigma^-)$ Emission in Comets

L. J. Stief and V. J. DeCarlo

The presence of NH radicals in the coma of comets has been generally attributed to photodissociation of ammonia. However, vacuum ultraviolet photolysis¹ ($1236\overset{\circ}{\text{\AA}}$) of ammonia results in emission at $3240\overset{\circ}{\text{\AA}}$

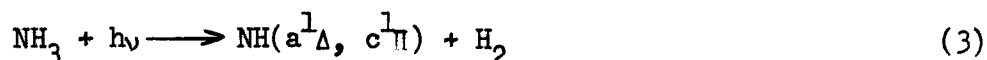


while the cometary emission at $3360\overset{\circ}{\text{\AA}}$ corresponds to

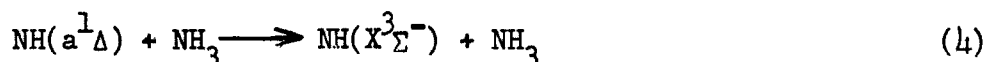


The energy level diagram for NH showing the position of the states and the transitions under discussion is shown in Figure 4-1. In the vacuum ultraviolet flash photolysis of ammonia,^{2, 3} the NH absorption band at $3360\overset{\circ}{\text{\AA}}$ ($\text{A}^3\Pi \leftarrow \text{X}^3\Sigma^-$) was observed.

These results may be explained³ by initial formation of NH in the singlet system



with collision-induced transformation to ground state NH.



Ground state NH could also be formed directly in decomposition of NH_3 .



Formation of $\text{NH}(\text{X}^3\Sigma^-)$ and H_2 is spin forbidden since the excited state of NH_3 formed upon absorption of light in the region $1220\text{--}1140\overset{\circ}{\text{\AA}}$ (state III)

Note: This section has been published under the above title in NATURE 205, 889 (1965).

1. K. H. Becker and K. H. Welge, Z. Naturforsch. 18a, 601 (1963).
2. K. D. Bayes, K. H. Becker, and K. H. Welge, Z. Naturforsch. 17a, 676 (1962).
3. F. Stuhl and K. H. Welge, Z. Naturforsch. 18a, 900 (1963).

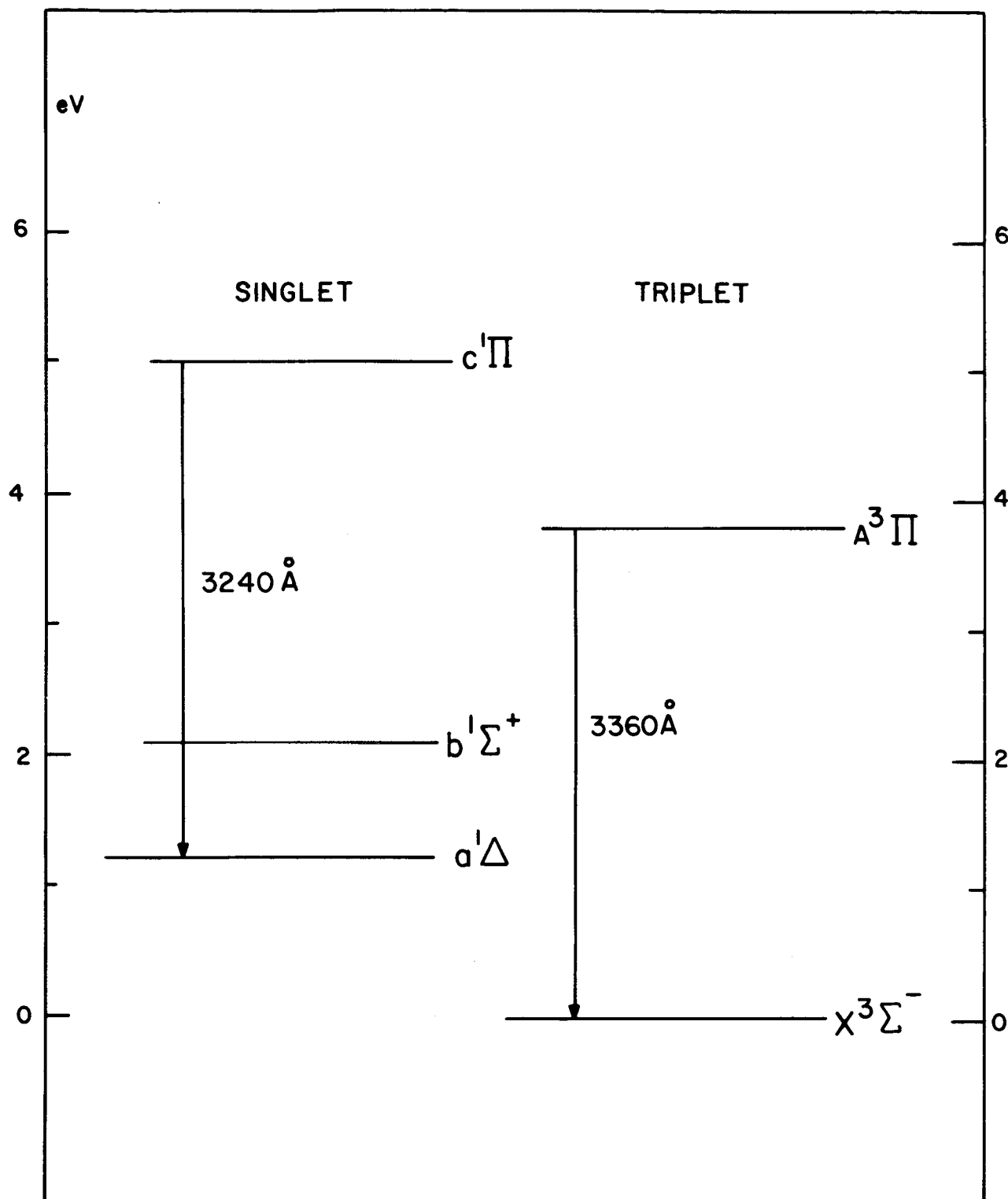


Figure 4-1. Energy Level Diagram of NH

is a singlet.⁴ Whatever the mechanism for production of ground state NH, it is evident that in photodecomposition of ammonia, NH is formed to some extent in the singlet system. Since the $a^1\Delta \longrightarrow X^3\Sigma^-$ is highly forbidden, $\text{NH}(a^1\Delta)$ will have a very long lifetime in the absence of collision with other molecules. Evidence for fact that radicals do not suffer collisions from the time of their formation near the nucleus until resonance fluorescence occurs further out in the coma comes from the observation that the C_2 radical shows a vibrational and rotational distribution which corresponds to a temperature of about 2500°K , while CN simulates a very low temperature distribution. A completely symmetrical molecule like C_2 has no permanent dipole and is therefore unable to emit vibrational and rotational energy. Energy may therefore be transferred only by collisions. The fact that C_2 retains excess vibrational and rotational energy suggests that it has suffered few if any collisions from the time of its formation to the time of its excitation by a fluorescence process. Thus, in the coma of a comet, considerable concentration of $\text{NH}(a^1\Delta)$ should accumulate if ammonia is the source of NH radicals. Emission from $\text{NH}(c^1\Pi)$ at 3240\AA by a fluorescence process should be observed in cometary spectra along with the 3360\AA emission from the triplet system of NH. Since only the 3360\AA emission is observed, an alternate source of NH radicals which produces only the triplet system on photodecomposition is required.

Recent results obtained in our laboratory on emission spectra from hydrazine vapor during photolysis at the krypton resonance lines (1236\AA

4. R. J. Thomson and A. B. F. Duncan, J. Chem. Phys. 14, 273 (1946).

and 1165 $\overset{\circ}{\text{\AA}}$) are pertinent to this problem. While the work was in progress, Becker and Welge reported⁵ results on the emission spectra during photolysis of hydrazine which are in complete agreement with our observations. When hydrazine, carefully purified of ammonia, is photolyzed at 50 μ Hg pressure, emission at 3360 $\overset{\circ}{\text{\AA}}$ is observed. This is undoubtedly the 0,0 band of the $A^3\Pi \longrightarrow X^3\Sigma^-$ NH transition. Emission is not observed at 3240 $\overset{\circ}{\text{\AA}}$ (0,0 band of the $c^1\Pi \longrightarrow a^1\Delta$ transition). Detection of emission at 3240 $\overset{\circ}{\text{\AA}}$ in the presence of emission at 3360 $\overset{\circ}{\text{\AA}}$ is within the resolution of our grating, and emission at 3240 $\overset{\circ}{\text{\AA}}$ amounting to a few percent of that at 3360 $\overset{\circ}{\text{\AA}}$ could have been detected. Thus, photodecomposition of hydrazine appears to produce NH radicals in the triplet system only. On this basis we would suggest that the immediate precursor of NH radicals in comets is hydrazine or a hydrazine-type molecule and that the role of ammonia in the comet model needs reconsideration.

5. K. H. Becker and K. H. Welge, Z. Naturforsch. 19a, 1006 (1964).

SECTION 5

VACUUM ULTRAVIOLET PHOTOLYSIS OF MIXTURES OF
METHANE AND WATER

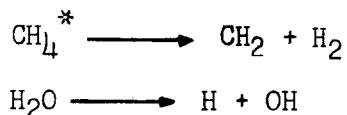
5. Vacuum Ultraviolet Photochemistry. II. Photolysis of Mixtures of Methane and Water

L. J. Stief and V. J. DeCarlo

5.1 Introduction

Many studies have been reported¹ on the production and identification of free radicals produced in the gas phase or at low temperatures in inert matrices. Very little work has been reported on the production of free radicals in reactive matrices. In this regard the work of Milligan^{2,3} where radicals are generated by photolysis and react with the matrix material is of note. The current investigation was interested in simultaneously producing radicals from both methane and water and studying the resultant chemical reactions.

The vacuum ultraviolet photolysis of methane and of water in the gas phase has been reviewed by McNesby and Okabe.⁴ The major primary process for these compounds are



It is also possible at these wavelengths to produce small concentrations of CH and CH₃ from methane and oxygen atoms from water.

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1. A. M. Bass and H. P. Broida, Formation and Trapping of Free Radicals, Academic Press, New York, 1960.
 2. D. E. Milligan et al, J. Chem. Phys. 37, 2302 (1962).
 3. D. E. Milligan, M. E. Jacox, J. Chem. Phys. 38, 2627 (1963).
 4. W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Advances in Photochemistry, Vol. 3, Interscience Publishers, New York, 1964.

NOTE: This work will be submitted for publication at a later date.

The low-temperature photolysis of methane at 20°K has been recently reported using 1237Å or 1470Å radiation and evidence is presented for the production of CH₂ and CH₃ radicals.⁵ However, no low-temperature studies on the photolysis of water in this wavelength region are available.

The existence and application of gas hydrates has been reviewed by Miller⁶ and studies using this matrix to study free radicals have been reported by Goldberg.⁷ The present investigation has studied the reactions of methane hydrates at -195°C at 1470Å and 1236Å and also of mixtures of methane and water at 25°C in the 1450Å to 1850Å region and at 1470Å and 1236Å. At 1470Å and 1236Å, the influence of reactive mixtures is made apparent by the unexpected formation of carbon monoxide and carbon dioxide.

5.2 Experimental

Light Sources and Actinometry

The Hanovia hydrogen discharge lamp, fitted with a sapphire window and operated at 450 milliamperes, provided effective radiation between 1450Å (sapphire cutoff) and 1850Å (absorption limit of water). The intensity of light absorbed in the reaction volume was estimated from the yield of CO from photolysis of CO₂.⁸ A typical value for the absorbed intensity is 4×10^{14} quanta/second.

5. P. Ausloos, R. E. Rebert, and S. G. Lias, J. Chem. Phys. 42, 540 (1965).

6. S. L. Miller, Proc. Nat'l. Acad. Sci. 47, 1798 (1961).

7. P. Goldberg, J. Chem. Phys. 40, 427 (1964).

8. D. Warneck, Disc. Faraday Soc., No. 37, p. 57 (1964).

The xenon and krypton resonance lines were excited in an air-cooled electrodeless discharge powered by a Raytheon 2450-MC microwave generator, the details of which are given elsewhere.⁹ The xenon and krypton lamps were fitted with freshly polished LiF windows. Contributions from the weaker Kr (1165Å) and Xe (1295Å) lines have not been included in estimating relative absorption by methane and water. The krypton lamp had no photochemical effect on water or carbon dioxide when each were exposed in a cell fitted with a sapphire window. This indicates that no effective radiation above 1450Å was emitted by the lamp. Light intensities as determined by CO₂ actinometry⁸ were usually in the range 10¹⁵ to 10¹⁶ quanta/second.

Relative absorption by methane and water in the gas-phase experiments was estimated from the pressure of each gas used and the absorption coefficients¹⁰ at 1236Å and 1470Å. It was assumed that CH₄ was completely transparent in the region of wavelengths emitted by the hydrogen discharge lamp fitted with a sapphire window. For experiments in the solid phase, the data of Dressler and Schnepf¹¹ was employed, although it is realized that the structure of the methane-water hydrate at -196°C may be quite different from the structure of the pure solids used by these authors. Also, no estimate could be made on losses due to scattering from the solid. Thus the relative absorptions by CH₄ given later in Table 5-3 are to be taken as rough, qualitative guides rather than quantitative estimations.

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9. L. J. Stief, V. J. DeCarlo and R. J. Mataloni, J. Chem. Phys. (in press) (1965).
 10. K. Watanabe, M. Zelikoff and E. C. Y. Inn, "Absorption Coefficients of Several Atmospheric Gases," Geophysical Research Paper No. 21, Geophysics Research Directorate, Air Force Cambridge Research Center, Cambridge, Mass., June 1953.
 11. K. Dressler and O. Schnepf, J. Chem. Phys. 33, 270 (1960).

Materials

Phillips research-grade methane (99.99% pure) was used. The major impurity was ethane which was reduced from a value of 0.02% or higher to less than 10 ppm by repeated cycles of pumping and trap-to-trap distillation. The "purified" methane still contained 0.5% N_2 and 0.1% Ar, but these are not likely to interfere in the reaction. The level of O_2 impurity was below 10 ppm. Methane - d_4 was obtained from Merck, Sharpe and Dohme, Ltd., Montreal, and used without further purification.

Water was obtained by dehydration of reagent-grade copper sulfate hexahydrate and stored in a quartz tube on a vacuum line. H_2O^{18} (91.28% O^{18} and 0.49% O^{17}) was obtained from Isomet Corporation, Palisades Park, New Jersey. D_2O (99.5% pure) was obtained from Hazleton Nuclear Science Corp., Palo Alto, California. All were purified further by continued pumping and thawing at $-80^\circ C$ to remove dissolved CO_2 .

Krypton, xenon, carbon dioxide, and carbon monoxide were obtained from Air Reduction Company, Jersey City, New Jersey and used without further purification.

Procedure

A mercury-free vacuum system equipped with stopcocks greased with Apiezon-N grease was employed. Pressures in the gas reaction cell or in the Dewar volume were measured with a CVC Autovac gauge which had been calibrated against a Trans Sonics capacitance manometer for each gas used.

For the gas-phase experiments, a 100 cc cylindrical Pyrex reaction cell equipped with a 25 mm LiF window was used. This cell contained a small solenoid-operated circulator for the circulation of gases. Reactants were mixed for 30 to 60 minutes prior to photolysis, and circulation

was continued during the photolysis. The gases which were non-condensable at -196°C were collected after circulating the mixture for 45 minutes through a trap maintained at this temperature. Blank runs showed that this procedure was effective in removing water vapor from the gas stream. The gases which were condensable at -196°C but non-condensable at -80°C were also collected. Analysis of both fractions was performed in a CEC 21-130 mass spectrometer.

For the solid-phase experiments, mixtures of the gases were prepared in the cell used for gas-phase photolysis, circulated for 45 minutes, and deposited slowly over a period of about two hours onto a 25 mm diameter circular Pyrex deposition surface maintained at -196°C . The surface containing the deposit was then rotated 180° from a position in front of the deposition arm to a position in front of a 25 mm LiF entrance window. The Dewar was made entirely of Pyrex and had an internal volume of 125 cc. The distance between the LiF window and the deposition surface was kept to 7 mm. This was done in order to minimize photolysis of product gases that could be evolved from the solid during the reaction. The samples which were collected included (a) gases present over the solid after photolysis, (b) gases which were non-condensable at -196°C after warming to melt the deposit and re-cooling to -196°C , and (c) gases which were condensable at -196°C but non-condensable at -80°C . All fractions were analyzed in the CEC 21-130 mass spectrometer.

5.3 Results

Gas-Phase Photolysis

The gas-phase photolysis of methane and water mixtures was carried out in the $1450\text{\AA} - 1850\text{\AA}$ region and at 1470\AA and 1236\AA . The unexpected

formation of carbon monoxide and carbon dioxide was found to occur at 1470Å and 1236Å. To obtain information on the manner of the formation of these products, additional experiments were performed with mixtures of $\text{CH}_4 + \text{D}_2\text{O}$, $\text{CD}_4 + \text{H}_2\text{O}$, $\text{CH}_4 + \text{H}_2\text{O}^{18}$, and $\text{CO} + \text{H}_2\text{O}$ and with pure H_2O and D_2O .

Photolysis at 1470Å and 1236Å

The results at these wavelengths were quite similar and will be discussed together. The major products observed were H_2 , C_2H_6 , CO , and CO_2 . In the experiments at 1470Å, the fraction of radiation absorbed by methane was almost negligible, while appreciable absorption by methane occurred at 1236Å. The estimates given in the text and in the tables, do not take into consideration any differences in absorption between different isotopically substituted molecules.

Methane and Water - Analysis of the products from the photolysis of $\text{H}_2\text{O} + \text{CH}_4$ mixtures showed the presence of CO and CO_2 . To positively identify these as products of the reaction, $\text{H}_2\text{O}^{18} + \text{CH}_4$ mixtures were photolyzed. These experiments yielded new m/e peaks corresponding to CO^{18} , CO_2^{18} , and $\text{CO}^{16}\text{O}^{18}$.

The effect of conversion on various product ratios is shown in Table 5-1. To correct for possible variations in lamp intensity and window transmittance from one experiment to the next, CO and CO_2 have been considered with reference to the C_2H_6 formed in the photolysis. It is evident that with increasing conversion of the reactants, CO decreases, CO_2 increases, but the sum of the two products does not appear to be affected.

Table 5-1

Effect of Conversion on Various Product Ratios in
Photolysis of 18 mm H₂O¹⁸ and 3 mm CH₄ at 25°C

λ (Å)	Time (min)	CO/C ₂ H ₆	CO ₂ /C ₂ H ₆	CO + CO ₂ /C ₂ H ₆
1470 ^(a)	60	1.6	0.9	2.5
1470 ^(a)	97	0.6	1.2	1.8
1470 ^(a)	150	0.7	2.0	2.7
1236 ^{(b)(c)}	95	1.2	1.2	2.4
1230 ^(b)	15	0.7	2.0	2.7
1236 ^(b)	30	0.5	2.1	2.6

(a) 0.3% of light absorbed by CH₄

(b) 25% of light absorbed by CH₄

(c) This experiment performed at about one-tenth lower light intensity.

The effect of the water-to-methane ratio on the product ratio CO+CO₂/C₂H₆ has not been examined quantitatively in the gas-phase experiments. However, experiments at 1470Å and 1236Å with 18 mm H₂O and 50 mm CH₄ (4.4% and 85% absorption by CH₄ respectively) indicated that in going from 3 to 50 mm CH₄, the ratio CO+CO₂/C₂H₆ is decreased by a factor of 10 to 100. This is not inconsistent with a linear relationship between H₂O/CH₄ and CO+CO₂/C₂H₆ in the range indicated. A strong dependence between the ratio of products and ratio of the reactants is quite evident.

No analysis has been attempted for products condensable at -80°C. The CO₂ and C₂H₆ account for about 80% of the products removed at -80°C and the presence of other compounds in this fraction is suggested by the

consistent observation of peak residues at $m/e = 28$ and 29 . When H_2O^{18} was substituted for H_2O , the peak residues appeared at $m/e = 29$ to 32 . Replacing CH_4 with CD_4 gave residues at $m/e = 31$ and 32 . Replacing H_2O with D_2O resulted in the same peak residues ($m/e = 28$ and 29) as obtained for H_2O . These shifts suggest the presence of a compound containing C, H, and O, with the hydrogen coming only from the methane.

Methane and D_2O - Photolysis of 18 mm D_2O and 3 mm CH_4 at $25^\circ C$ resulted in the formation of isotopically substituted methanes. The distribution obtained from these experiments is shown in Table 5-2.

Table 5-2

Production of Isotopically Substituted Methanes in the
Photolysis of 18 mm D_2O and 3 mm CH_4 in Gas Phase at $25^\circ C$

Lamp	Principal Wavelength	% Absorption by CH_4	Relative Amount				
			CH_4	CH_3D	CH_2D_2	CD_3H	CD_4
H_2 discharge	1450-1850 \AA	-0-	100	0.1	<0.05	<0.02	<0.02
Xe resonance	1470 \AA	0.3	100	2.8	1.1	0.4	0.2
Kr resonance	1236 \AA	25	100	2.9	1.7	0.7	0.2

Photolysis at 1470 \AA - 1850 \AA

In this wavelength region mixtures of $CH_4 + H_2O$, $CH_4 + D_2O$, $CO + H_2O$ were studied. For comparison, pure H_2O and D_2O were also studied. The major products formed from the mixtures of $CH_4 + H_2O$ at this wavelength were H_2 and C_2H_6 .

Methane and Water - In the photolysis of methane-water mixtures at $25^\circ C$, ethane and hydrogen were the major products. The time dependence of the ethane yield from the photolysis of 18 mm H_2O in the presence of 30 mm CH_4 at $25^\circ C$ is shown in Figure 5-1. The effect of methane pressure on the ethane yield at a constant reaction time of 30 minutes is shown in

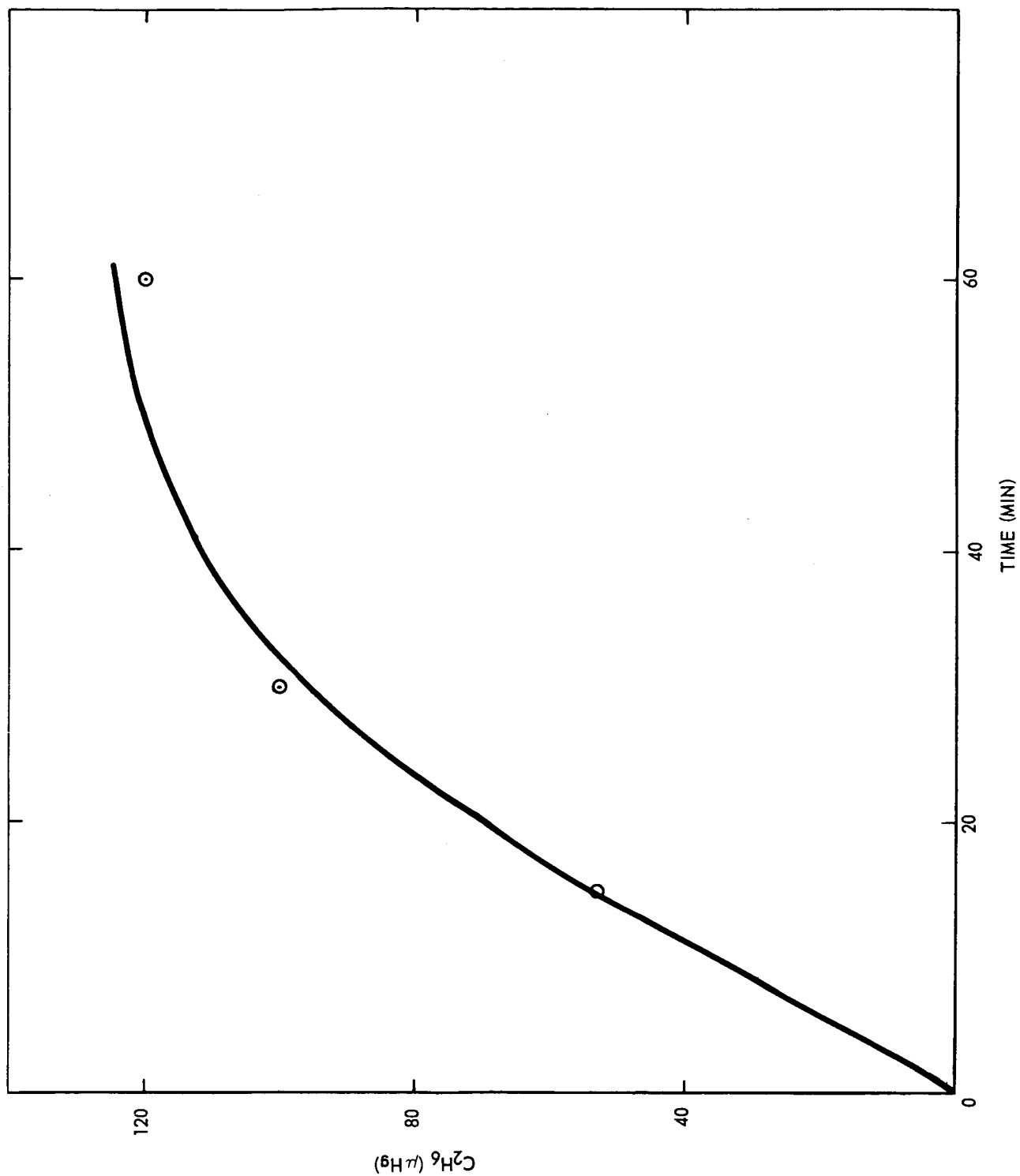


Figure 5-1. Yield of Ethane in Photolysis of 18 mm H_2O in the Presence of 30 mm CH_4 Using a Hydrogen Discharge Lamp

Figure 5-2. Absorption of light by methane was negligible in these experiments. The quantum yield for the formation of ethane is estimated to be 0.6.

Methane and D₂O - In the photolysis of 18 mm D₂O in the presence of 3 mm CH₄, no evidence was obtained for the formation of isotopically substituted methanes as in 1236⁰Å and 1470⁰Å photolysis.

Carbon Monoxide and Water - Photolysis of 18 mm H₂O in the presence of 100 u of CO at 25°C resulted in CO₂ formation at the rate of 0.24 u/minute. Addition of 3 mm CH₄ to this system reduced the rate of CO₂ production to 0.18 u/minute.

Water, D₂O - The hydrogen yield from the photolysis of 18 mm water vapor at 25°C is shown in Figure 5-3 as a function of photolysis time. The rate of hydrogen production was determined from the slope of the linear portion of the plot and the average of several such determinations leads to a quantum yield of 0.40 ± 0.01 . The quantum yield for deuterium production from D₂O under identical conditions is 0.32 ± 0.01 , but if all the hydrogen is included, i.e. D₂, HD, and H₂, the quantum yield is 0.40 ± 0.01 . No evidence was obtained for oxygen formation in these experiments.

Photolysis of Solids at -196°C

The photolysis of the methane-water hydrate at -196°C was studied only at 1236⁰Å and 1470⁰Å. The products which were obtained included H₂, CO, CO₂, and C₂H₆. Use of H₂O¹⁸ resulted in the observation of CO¹⁸, CO₂¹⁸, and CO¹⁶O¹⁸. Limited experiments were also carried out on mixtures of CO + H₂O¹⁸ to investigate possible production of CO₂ at low temperatures. The results are presented below by consideration of the reaction products.

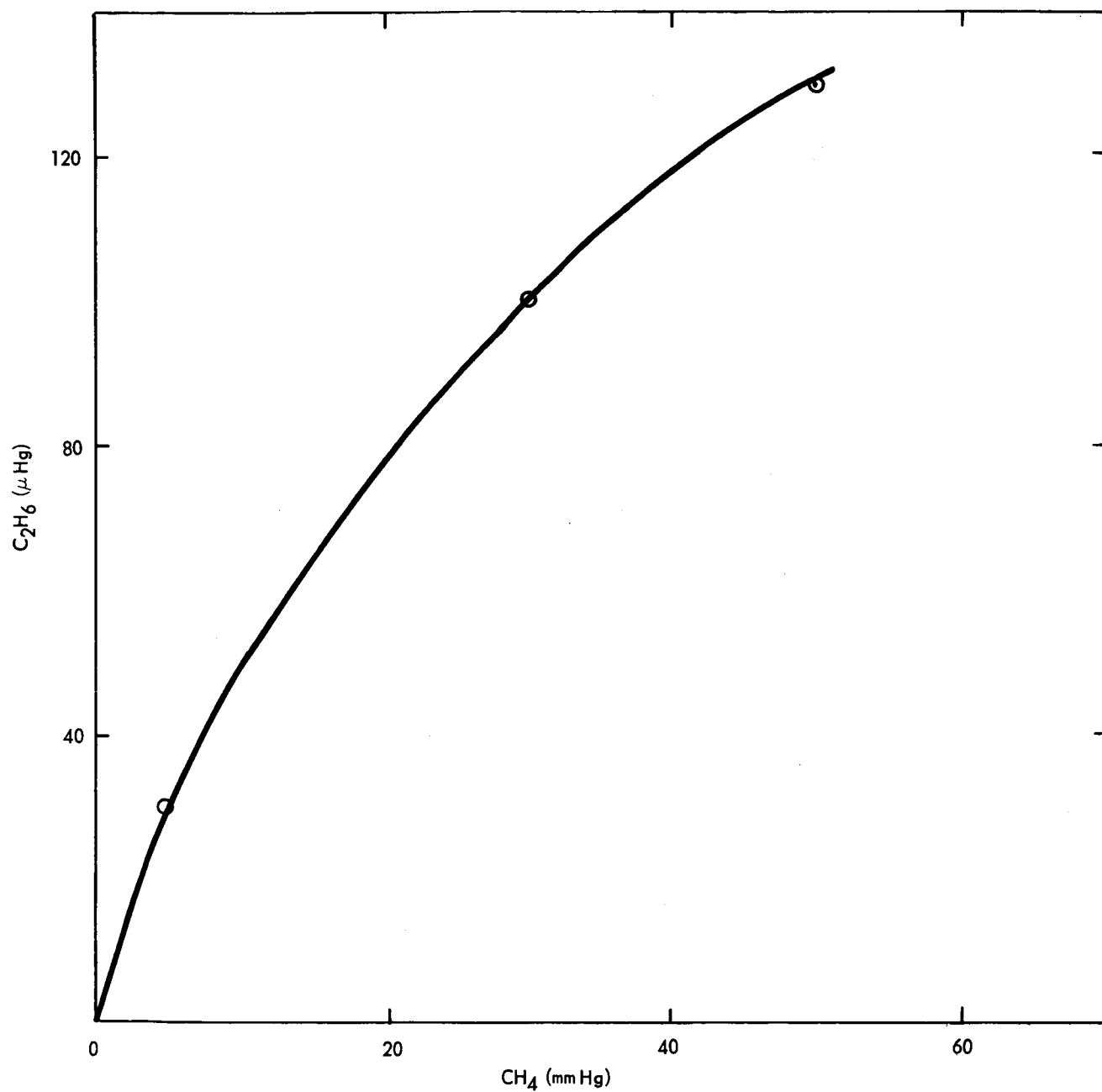


Figure 5-2. Effect of Methane on Yield of Ethane Using Hydrogen Discharge Lamp. Pressure of Water = 18 mm; Reaction Time = 30 min.

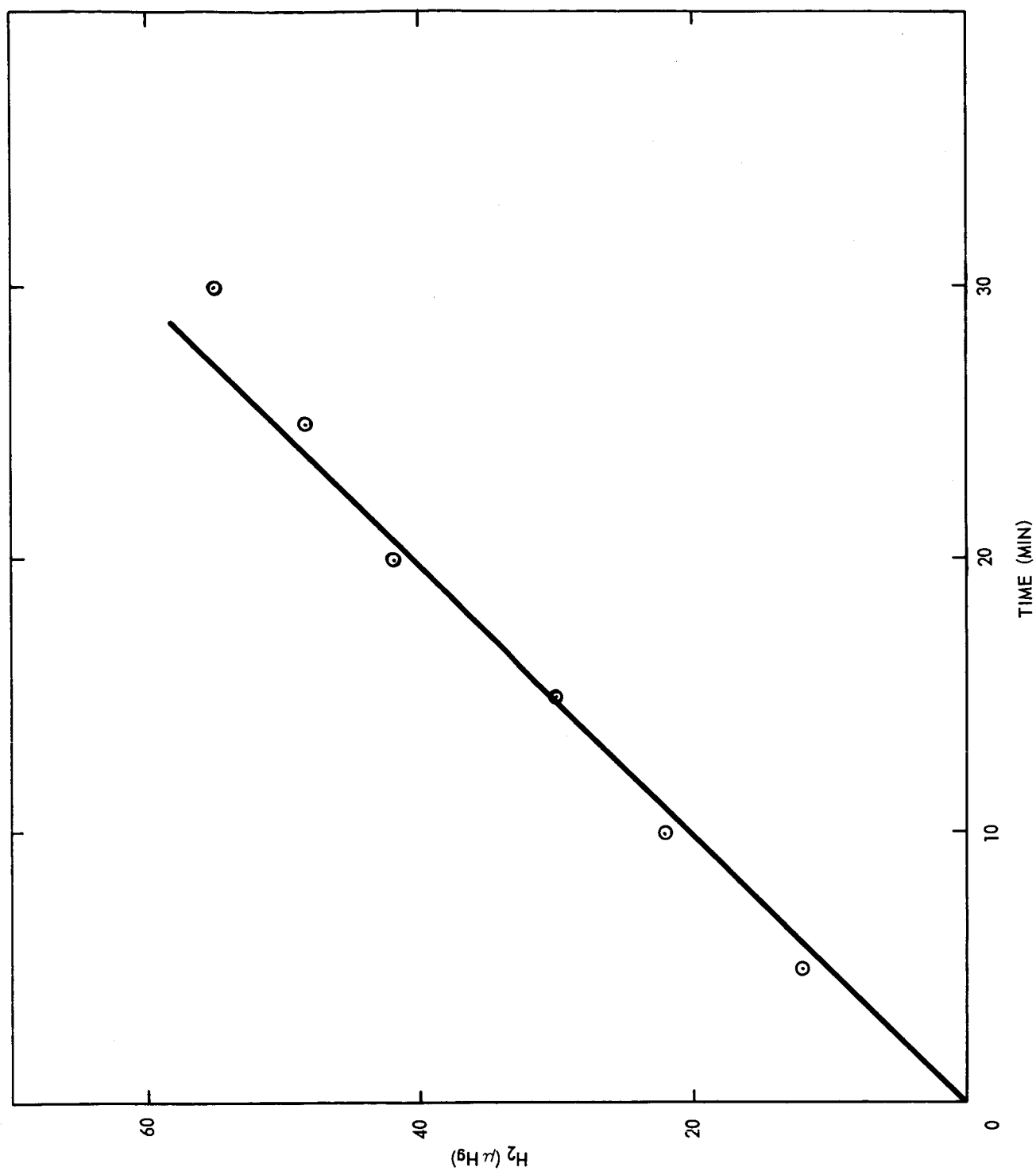


Figure 5-3. Yield of Hydrogen from the Photolysis of Water Vapor at 25°C Using a Hydrogen Discharge Lamp

Hydrogen

The production of hydrogen from the photolysis of H_2O at -196°C was extremely low compared to the production from the vapor at 25°C . The addition of CH_4 (at 1236\AA) or CO (at 1470\AA and 1236\AA) to D_2O resulted in a ten- to 50-fold increase in D_2 production.

In the photolysis of $\text{CH}_4 \cdot 6\text{D}_2\text{O}$ and of $\text{CD}_4 \cdot 6\text{H}_2\text{O}$ at 1236\AA the hydrogen produced (almost entirely in the vapor phase over the photolyzed solid and not entrapped in the deposit) was predominantly H_2 and D_2 , respectively. That is, the major portion of hydrogen produced in the photolysis of the methane-water clathrate came from the methane despite the fact that methane probably absorbs less than one-third of the radiation at 1236\AA .

Carbon Dioxide and Ethane

The CO_2 and C_2H_6 produced by photolysis of $\text{CH}_4 \cdot x\text{H}_2\text{O}$ with 1236\AA radiation is shown in Table 5-3. The effect of photolysis time has been examined for $\text{H}_2\text{O}/\text{CH}_4$ ratios of 72 and six. In both instances, the ratio $\text{CO}_2/\text{C}_2\text{H}_6$ appears to be essentially independent of reaction time. The actual amounts of both CO_2 and C_2H_6 increase with time but apparently at a decreasing rate.

The effect of changing the ratio of the reactants ($\text{H}_2\text{O}/\text{CH}_4$) on the ratio of the products ($\text{CO}_2/\text{C}_2\text{H}_6$) using 1236\AA is shown in Figure 5-4. It may be seen that $\text{CO}_2/\text{C}_2\text{H}_6$ is a linear function of $\text{H}_2\text{O}/\text{CH}_4$ with the intercept at the origin.

To increase the amount of products both the thickness of the deposit and mode of deposition was varied. The effect of increasing the deposit thickness was examined for a $\text{H}_2\text{O}/\text{CH}_4$ ratio of 18. Increasing the amount

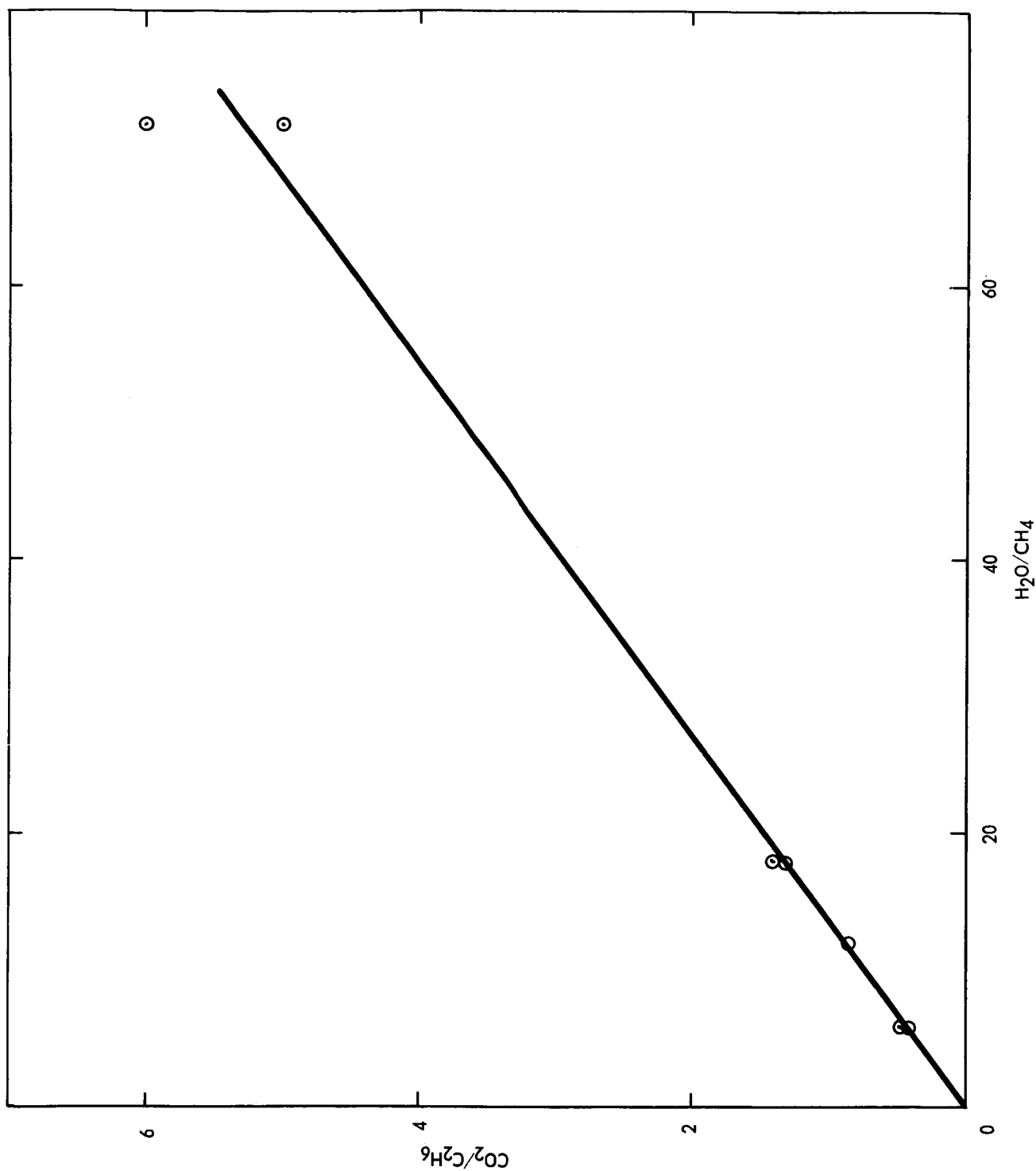


Figure 5-4. Relationship Between Ratio of Products ($\text{CO}_2/\text{C}_2\text{H}_6$) and Ratio of Reactants ($\text{H}_2\text{O}/\text{CH}_4$) in the Photolysis of Methane Hydrate at 77°K and 1236Å

Table 5-3

Formation of CO_2 and C_2H_6 in Photolysis of the
Methane Hydrate ($\text{CH}_4 \cdot x\text{H}_2\text{O}$) at 77°K and 1236\AA

"x" $\text{H}_2\text{O}/\text{CH}_4$	% Absorption ^(e) by CH_4	Reaction Time (min)	Pressure in Reaction Volume (u Hg)		$\text{CO}_2/\text{C}_2\text{H}_6$
			CO_2	C_2H_6	
72	3	30	9	1.5	6.0
72	3	120	11.5	2.3	5.0
18	14	30	13.5	9.5	1.4
18 ^(a)	14	30	14	11	1.3
12	21	30	15	17.5	0.86
6	30	30	2.9	6.5	0.45
6	30	120	6.0	15	0.40
6 ^(b)	30	30	4.8	10.2	0.47
6 ^(c)	0.01	30	2.8	10	0.28
6 ^(d)	30	15	8	20	0.40

(a) Three times normal size deposit

(b) Normal size deposit laid down in three steps with
subsequent ten minute photolysis of each fresh deposit

(c) Photolysis at 1470\AA

(d) H_2O^{18} used; pressure of CO^{18} in reaction volume = 12u

(e) Based on absorption measurements of Dressler and Schnepf;¹¹
qualitative guide only; see experimental section

of deposited material by a factor of three had no effect on ratio of CO_2 to C_2H_6 nor on actual amounts of these gases produced in the photolysis. The effect of renewing the surface of the deposit while keeping the final size of deposit and total reaction time to the usual levels was examined

at a $\text{H}_2\text{O}/\text{CH}_4$ ratio of six. While the ratio $\text{CO}_2/\text{C}_2\text{H}_6$ remained unchanged, a 50% increase in amount of product formed was observed. All these effects on the amount of product formed indicate that photochemical decomposition takes place in a relatively thin layer on the surface of the deposit.

For a $\text{H}_2\text{O}/\text{CH}_4$ ratio of six, the product ratio $\text{CO}_2/\text{C}_2\text{H}_6$ appears to be lower for photolysis at 1470\AA as compared to photolysis at 1236\AA .

CO_2 Formation in $\text{H}_2\text{O}^{18} + \text{CO}$ Photolysis

A mixture of 18 mm H_2O^{18} and 500 u CO was slowly deposited onto a surface at -196°C . Only about half the CO was entrapped in the solid; the CO remaining in the vapor phase was pumped away. Photolysis of this deposit at 1470\AA and 1236\AA resulted in the formation of $\text{CO}^{16}\text{O}^{18}$ at rate of 0.26 u/minute.

5.4 Discussion

The results obtained in the gas-phase photolysis of H_2O and D_2O using a hydrogen discharge lamp are in agreement with those recently published by Ung and Back¹² for photolysis at 1849\AA . These include the quantum yield measurements of 0.4 for hydrogen or deuterium production from H_2O and D_2O , respectively, and the observation that the rate of hydrogen production decreases with time as shown in Figure 5-1. The primary process for water vapor photolysis in the first continuum, which is consistent with these results, is given by Reaction (1)



12. A. Y-M, Ung and R. A. Back, Can. J. Chem. 42, 753 (1964).

The addition of CH_4 to this system results in the production of ethane. Since CH_4 is transparent at these wavelengths, the occurrence of the reaction



followed by



is suggested. The dependence of the rate of ethane formation on methane pressure (Figure 5-3) and the estimated quantum yield for ethane formation of 0.6 are consistent with the occurrence of Reactions (2) and (3).

At 1236\AA it has been shown by McNesby, Tanaka, and Okabe¹³ that, in addition to Reaction (1), Reaction (4) can occur with one-third the probability of (1)



For methane, the primary process in this wavelength region is



The occurrence of (4) in the photolysis of water at 1470\AA has recently been demonstrated¹⁴ to occur with about one-sixth the probability of (1).

From these results the photolysis of a mixture containing methane and water would be expected to produce the radicals H, O, OH, CH_3 , CH_2 with 1236\AA radiation; H, O, CH_3 , OH radicals with 1470\AA ; and H, CH_3 , OH radicals with radiation $> 1500\text{\AA}$. In the current work, the results obtained using 1470\AA and 1236\AA were similar to each other but quite

13. J. R. McNesby, I. Tanaka, and H. Okabe, J. Chem. Phys. **36**, 605 (1962).
 14. L. J. Stief, unpublished results.

different from those obtained in identical experiments using a hydrogen discharge lamp. At 1236\AA and 1470\AA the observed products of the photolysis of the methane-water mixtures were CO , CO_2 , C_2H_6 , and H_2 while with the hydrogen discharge lamp, only H_2 and C_2H_6 were obtained.

The photolysis of water at -196°C was found to be very resistant to photochemical decomposition using 1236\AA or 1470\AA radiation. Estimates of the maximum level of hydrogen production are from 1 to 0.1% of the rate observed in the gas-phase photolysis. The lower value is based on production of D_2 from D_2O . This indicates that if water dissociates into H and OH , cage recombination of these radicals probably occurs.

When CH_4 or CO are present in the solid water matrix, the hydrogen yield increases by a factor of five to 50. Under these conditions any radicals produced from H_2O can readily react with a close CH_4 or CO molecule. When CH_4 is in the solid, C_2H_6 , CO , and CO_2 products are also found. These products are identical to those obtained in the gas-phase experiments at these wavelengths and are most likely produced by the same reactions. When CO is present in solid water matrix, CO_2 is obtained as a product, indicating this reaction has a very low activation energy.

CO_2 Formation

The photolysis of methane and water mixtures with 1470\AA or 1236\AA radiation yields as major products H_2 , C_2H_6 , CO , and CO_2 . The decrease of CO with reaction time and increase in CO_2 is evidence for the production of CO_2 from CO . Reaction (6) appears to be the most reasonable explanation for CO_2 formation.



Based on a value^{12,15,16} of $k_2/k_6 = 0.6 \times 10^{-3}$, it may be estimated that with as little as 10 u of CO from photolysis, the rate of reaction of OH with 3 mm CH₄ is only 1/5 as fast as the reaction of OH with CO. In the later stages of the reaction as the pressure of CO increases, reaction of OH with CH₄ will be even less favored. Thus the occurrence of (6) is quite consistent with ratios of reactants employed and amount of product formed in photolysis of a mixture of 18 mm H₂O and 3 mm CH₄. Since values for E_6 of 2 or 7 kcal/mole have been suggested,^{15,17} it may be of interest to note that our demonstration that Reaction (6) occurs in the solid at -196°C is more consistent with a low value for E_6 .

Other reactions that could be responsible for CO₂ production are



The occurrence of reaction (7a)¹⁸ is not consistent with the relative concentrations of CO, CH₄, and H₂O formed in these experiments and the known absorption coefficients¹⁰ of these molecules. It is known that for O(³P) atoms Reaction (8) is very slow,¹⁹ and from the results

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15. C. D. Fenimore and G. W. Jones, J. Phys. Chem. **65**, 2200 (1961).
 16. D. E. Hoare, Nature **194**, 283 (1962).
 17. L. I. Avarmenko and R. V. Kolesnikova, "Mechanism and Rate Constants of Elementary Gas Phase Reactions Involving Hydroxyl and Oxygen Atoms," Advances in Photochemistry, Vol. 2, 25, Interscience Publishers, New York, 1964.
 18. W. Groth, W. Ressler and H. J. Rommel, Z. Physik. Chem. (Frankfurt), **32**, 192 (1962).
 19. F. Kaufman, "Reactions of Oxygen Atoms," Progress in Reaction Kinetics, Vol. I, Pergamon Press, London, 1961.

obtained in the photolysis of CO_2



it is expected that the reaction of $\text{O}(^1\text{D})$ with CO is not very important.

CO Formation

The reactions responsible for the production of CO are the most difficult to identify in this study. Reactions producing CO occur both with 1236\AA and 1470\AA radiation but not with the hydrogen discharge lamp. Several other differences were found for these two wavelength regions: (a) oxygen atoms (most likely $\text{O}(^1\text{D})$ atoms) can be produced with 1236\AA and 1470\AA radiation but probably not with the hydrogen discharge lamp, (b) mixture of $\text{CH}_4 + \text{D}_2\text{O}$ yields isotopically substituted methanes with 1236\AA and 1470\AA radiation but not with the hydrogen discharge lamp.

Since relative absorption by CH_4 is significant only at 1236\AA , reactions of species formed in the photodecomposition of CH_4 cannot be the deciding factor for the production of CO or the deuterated methanes.

The formation of methylene radicals is strongly suggested for the photolysis at 1470\AA and 1236\AA . Methyl radicals are known to be present when a hydrogen discharge lamp is used for the photolysis of a water-methane mixture. However, CO or deuterated methanes are not formed under these conditions. Since photolysis at the lower wavelengths does lead to CO and the deuterated methanes, the reactive species probably is the methylene radical.

The suggested importance of the occurrence of $\text{O}(^1\text{D})$ reactions at 1470\AA and the suggested presence of CH_2 radicals in the absence of CH_4 photodecomposition are consistent with the occurrence of the following reaction:



The subsequent reactions of CH_2 may be considered in terms of



where excited formaldehyde may decompose, at least partially, to CO . If Reaction (11b) is followed by (6) producing CO_2 , we may consider CO_2 as a correction to the CO yield. It then follows that:

$$\frac{R_{\text{CO}} + \text{CO}_2}{R_{\text{C}_2\text{H}_6}} = \frac{k_{11} \text{H}_2\text{O}}{k_{12} \text{CH}_4}$$

This requires that the ratio $\text{CO} + \text{CO}_2 / \text{C}_2\text{H}_6$ will (a) vary directly as the ratio $\text{H}_2\text{O}/\text{CH}_4$, (b) be the same for 1470\AA and 1236\AA provided CH_2 radicals are present in the system, and (c) be independent of reaction time. The last two requirements are met in our system and the first is fairly consistent with our limited findings on the effect of H_2O to CH_4 ratio.

If the ratio $\text{CO} + \text{CO}_2/\text{C}_2\text{H}_6$ does indeed represent the competition between the reaction of CH_2 with H_2O and with CH_4 , it may be estimated from the present results that methylene radicals react at least twice as fast with methane as with water.

Other potential sources of CO and C_2H_6 are:



It would be difficult to distinguish between formation of CH_2O^* by Reaction (13) and its formation by the sequence of Reactions (10) and (11).

While the suggested occurrence of Reaction (10) is quite tentative, it can be said with some certainty that the occurrence of some reaction involving oxygen atoms and the presence of CH_2 at both 1236\AA and 1470\AA is strongly suggested in these experiments.

Acknowledgement

The authors wish to thank Mr. John Hillman for performing some of the experiments and to express their indebtedness to consultations with Dr. James R. McNesby and Dr. Arnold M. Bass.

SECTION 6
THE CHEMISTRY OF COMETS
An Annotated Bibliography

FOREWORD

All investigations of cometary phenomena are directed toward the elucidation of the origin, formation, and evolution of comets which will, in turn, lead to a better understanding of the origin, formation, and evolution of the Solar System. Such investigations have encompassed many disciplines and recent advances in the fields of low-temperature physics and chemistry, photochemistry, magnetohydrodynamics, charge-transfer reactions, and scattering phenomena may hasten the ultimate explanation of cometary phenomena.

The multitude of astronomical observations made in the past have allowed the analysis of the observed cometary spectra and the tabulation of the physical properties and behavior of comets. From this data, notable experimental and theoretical studies have evolved.

The experimental studies have been pointed primarily toward an explanation of the occurrence of the observed emissions. Many preliminary assignments of cometary spectra have been verified by definite identification of the emitting species through laboratory investigation. With this done, the experimental studies have been aimed toward an explanation of the chemical processes and mechanisms responsible for the formation of the emitting species.

Various theoretical studies of cometary phenomena have been advanced to explain the existence of the nucleus, the mechanisms which produce the coma, and the properties of the tail. Such theories have described the nucleus, coma, and tail in terms of structure, composition, temperature, evaporation, photodecomposition, and interaction with protons, electrons, and radiowaves.

However, these theories must remain speculative as they have not, as yet, been wholly verified by experimental data.

In this respect, continued investigations in the chemistry of comets will be an invaluable tool in determining (1) the nature, concentration, ionization, and dissociation of the parent molecules of the emitting species in the coma and tail, (2) the release mechanisms responsible for the existence of the parent molecules, and (3) the composition of the nucleus.

The references included in this bibliography were accumulated at Melpar, Inc., during the course of Contracts NASw-589 and NASw-890, a program in comet chemistry directed toward the determination of the parent compounds responsible for the emissions observed in cometary spectra. Thus, all references reflect these investigations in their subject matter or represent the necessary background knowledge.

For convenience, the references are divided into three areas - (1) those which report the results of land-based observations and the theoretical interpretations resulting from these observations, (2) those which report data obtained in the laboratory as a direct result of experimentation, and (3) those which may indicate the trend of our future space investigations.

The availability of the Government contract reports is indicated when practical or necessary by the "N", "OTS", or "AD" numbers given after the reference. These numbers refer to the library indexes of the National Aeronautics and Space Administration, The Office of Technical Services, and the Defense Documentation Center, respectively.

Both an author index and a chemical index have been added to the bibliography for the user's convenience. The chemical index includes those chemical species cited in the abstracts and titles of the publications. The authors feel that, while no bibliography can claim to be complete, this compilation will provide a good basis for anyone interested in undertaking a study in the chemistry of comets.

The Chemistry of Comets -- An Annotated Bibliography

J. B. Evans and V. J. DeCarlo

OBSERVATIONS AND INTERPRETATION

1. B. M. Middlehurst and G. P. Kuiper (Editors)
THE SOLAR SYSTEM. VOL. IV. THE MOON, METEORITES, AND COMETS
The University of Chicago Press, Chicago, Ill., 1963

A comprehensive survey of information is contained in the six chapters devoted to comets and authored by noted authorities. Chapter 15 is authored by E. Roemer and deals with the discovery, orbits, and observation of comets; Chapter 16, by J. G. Porter, with orbital statistics; Chapter 17, by K. Wurm, with the physical and chemical properties and includes discussions of the form, spectra, excitation, densities, polarization, and mechanical theory; Chapter 18, by L. Biermann and Rh. Lust, with the structure and dynamics of cometary tails; Chapter 19, by F. L. Whipple, with the structure of the nucleus; and Chapter 20, by J. H. Oort, with empirical data on the origin of comets.

2. R. A. Lyttleton
The COMETS AND THEIR ORIGIN
Cambridge University Press, New York, N. Y., 1953

The properties and formation of comets are described in an effort to elucidate the origin of comets.

3. N. B. Richter
THE NATURE OF COMETS
Methuen and Company, Ltd., London, England, 1963

A translation of the original "Statistik und Physik der Kometen," the book provides a review of information concerning the history, statistics, theoretical models, structure, origin, formation, and decay of comets. Recent data obtained from the observations of Comets Arend-Roland and Mrkos and a chapter discussing future cometary investigations are also included.

4. P. W. Merrill
SPACE CHEMISTRY
The University of Michigan Press, Ann Arbor, Michigan, 1963

The chemistry of the solar system, stars, and nebulae is discussed and includes a short treatment of the chemistry of comets.

5. P. Swings
CONSIDERATIONS REGARDING COMETARY AND INTERSTELLAR MOLECULES
Astrophysical Journal 95, 270 (1942)

A comparative study is made of the possible mechanisms of formation, dissociation, and ionization in comets and in interstellar space. The additional identification work necessary to an explanation of these processes is set forth, while the identification, ionization, dissociation, and abundance of CH^+ , CN , and C_2 are treated at length.

6. P. Swings
MOLECULAR BANDS IN COMETARY SPECTRA. IDENTIFICATIONS
Rev. Mod. Phys. 14, 190 (1942)

A discussion summarizes the identification of the molecules OH , NH , CN , CH , C_2 , CH^+ , CO^+ , and N_2 . The source of these molecules and the problems associated with their identification are treated.

7. P. Swings
COMETARY SPECTRA. REPORTS ON THE PROGRESS OF ASTRONOMY
Monthly Notices of the Royal Astronomical Society 103, 86 (1943)

A review of cometary astronomy discusses the visible, ultraviolet, astronomical, and laboratory observation of the diatomic molecules OH , NH , and CH^+ ; the triatomic CH_2 ; and the less definite OH^+ and NH_2 . The previously identified molecules CN , C_2 , CH , CO^+ , and N_2 are also treated in a concluding discussion of the excitation mechanism and rotational structure of cometary bands, and of the physical form and stability of cometary materials.

8. P. Swings and T. Page
THE SPECTRUM OF COMET BESTER (1947k)
Astrophysical Journal 111, 530 (1950)

An analysis of the ultraviolet, visible, and near infrared spectra of Comet Bester (1947k) is presented with a summary of identifications for CN , C_2 , OH , NH , CO^+ , N_2^+ , OH^+ , NH_2 , and the $\lambda 4050$ band system. Molecules identified in the tail include CO^+ , and CO_2^+ , and the tentatively assigned NO and O_2 . Slit spectrograms of the tail cover the ultraviolet region, while spectrograms of the head cover the visible and near-infrared region. A comparison of this spectra with those of other comets is given, and the transitions and origin of the specific emissions are postulated.

9. T. Page
RECENT STATISTICAL STUDIES IN ASTRONOMY
Science 132, 1870 (1960)

Statistical studies reveal information about the mass, expansion, and radio emission of galaxies and the origin and loss of comets.

10. P. Swings and L. Haser
ATLAS OF REPRESENTATIVE COMETARY SPECTRA
The University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1956
AD 119 234

A compilation of 350 representative spectra is presented with description; notes, and references given as necessary. A foreword describes the meaningful aspects of cometary spectroscopy and includes definitions; instrumental influences; principles for the identification of emissions; wavelength tables; the cometary bands, continuum, molecules, etc; and the interrelation between cometary spectra and that observed in the atmosphere and stars.

11. P. Swings and L. Haser
NOTES ON COMETARY SPECTRA
The University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1956
AD 119 235

Notes published in addendum to Swing's Atlas explain the limitations effected by instrumental and observational errors and by the choice of comet model.

12. L. Haser
LA CONSERVATION DES RADICAUX LIBRES A' BASSE TEMPERATURE ET LA STRUCTURE DES NOYAUX DE COMETES
Comptes Rendus 241, 742 (1955)

It is theorized that the observed radicals are formed by photodissociation of the parent molecules produced by sublimation of the ices in the nucleus.

13. L. Haser
SUR LA PRODUCTION DES RADICAUX LIBRES DANS LES COMETES
Bull. Acad. R. Belg. 42, 80, 813 (1956)

A new process for the production of radicals by comets is proposed.

14. P. Swings
THE SPECTRA OF THE COMETS
Vistas in Astronomy 2, 958-981, Pergamon Press (1956)

A presentation of the general characteristics of comets is followed by a description of the ultraviolet, visible, and near infrared spectrum of the coma and tail. The assignment of the emissions is discussed along with the possible causes of excitation and the mechanisms.

15. P. Swings et al.
NOTES ON COMETARY PHYSICS
The University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1957
AD 117 169

Notes prepared preliminary to "Research on Relations between Cometary, Solar, and Atmospheric Physics," discuss the identification of emissions in cometary spectra, the possibility of fluorescence excitation in comets, the chemical reactions in comets, and the monochromatic intensity distribution in a comet's head.

16. P. Swings
RESEARCH ON RELATIONS BETWEEN COMETARY, SOLAR, AND UPPER ATMOSPHERIC PHYSICS
The University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1958
AD 152 525

An attempt to discover an interrelationship between cometary, solar, and atmospheric processes is presented in three sections. The section on cometary physics includes a number of studies: the assignment of the infrared system of CN, the identification of the forbidden lines of O(I) in comets and a comparison with that of the upper atmosphere, assignment of accurate wavelengths in the visible region and in particular for NH_2 , a comparison of Comet Encke in 1957 and 1947-1937, the origin of the continuous spectrum of comets, the intensity and polarization of light scattered by cometary particles, trapped radicals and their possible reactions, and the theoretical distribution of the molecules in the head.

17. P. Swings et al.
ON THE ORIGIN OF THE CONTINUOUS SPECTRUM OF COMETS
The University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1959
AD 243 271

The possible causes of the continuous spectrum of comets are examined. Four mechanisms are considered -- diffuse reflection by the solid nucleus, scattering by molecules, scattering by solid particles, and scattering by free electrons. It is concluded that the solar continuum of comets is due primarily to scattering by solid particles.

18. P. Swings et al.
RELATIONS BETWEEN COMETARY AND SOLAR ACTIVITY
The University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1960
AD 243 274

The behavior of dust and gaseous cometary heads is compared to solar activity to indicate that the brightness of a dust head is not related appreciably to solar activity while a gaseous head may be.

19. P. Swings
EXCITATION AND ABUNDANCES IN COMETS
University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1960
AD 243275

Cometary spectra are analyzed in studies of a fluorescence excitation mechanism for the C_2 Swan bands, the radii of the nuclei of the periodic Comets 1957c and 1959b, and the relative abundances of CO^+ in the tail and CN in the head of Comet Bester 1947k.

20. P. Swings, D. Bosman-Crespin and C. Arpigny
THEORETICAL CONSIDERATIONS ON THE PREDICTED FAR ULTRAVIOLET SPECTRA OF COMETS AND OF POLAR AURORAE
University of Liege, Institute of Astrophysics, Cointe-Schlessin,
Belgium, 1960
AD 257 098

The expected far ultraviolet spectra of comets and aurorae are discussed and specific predictions are tabulated for application to planned rocket and space probe investigation.

21. P. Swings
RECENT PROGRESS IN COMETARY SPECTROSCOPY
University of Liege, Department of Astrophysics, Cointe-Schlessin,
Belgium, 1963
AD 430 639

The report discusses recent progress in cometary observations and spectroscopy as well as in the understanding of the excitation mechanism of the diatomic and triatomic radicals and ions.

22. A. H. Delsemme and P. Swings
HYDRATES DE GAZ DANS LES NOYAUX COMETAIRES ET LES GRAINS INTERSTELLAR
Ann. d'Astrophys. 15, 1 (1952)

The presence of solid hydrates of CH_4 , CO_2 ,.... in cometary nuclei and interstellar grains is assumed and substantiated by noting that the vapor pressures of the various hydrates are of the same order of magnitude, while the vapor pressures of solid CH_4 , H_2O etc. differ by very large factors.

23. P. D. Jose and P. Swings
THE SPECTRUM OF COMET 19481
Astrophysical Journal 111, 41 (1950)

From an analysis of eight spectrograms of Comet 19481, sodium emission is identified at $r = 0.73$ and $r = 0.79$ AU, and CN and the $\lambda 4050$ group at $r = 2.21$ AU. The usual complex structure of the CN bands is attributed to the fluorescence excitation by solar radiation. The behavior of CH and " CH_2 " are compared, and unidentified features observed within and between the Swan bands and in the yellow-red region are discussed.

24. P. Swings et al.
RESEARCH ON RELATIONS BETWEEN COMETARY, SOLAR AND UPPER ATMOSPHERIC PROCESSES
University of Liege, Department of Astrophysics, Cointe-Schlessin, Belgium, March 31, 1964
AD 601 136

This report presents a discussion of the progress achieved in a program for the laboratory production of molecules of astronomical interest; study of the physical mechanisms of comets and the upper atmosphere; and investigations related to space experiments, which include far ultraviolet spectra of stars, comets and aurorae, and artificial comets.

25. L. Houziaux
DENSITY OF C_2 MOLECULES IN THE HEAD OF COMET MRKOS 1955e
The University of Liege, Institute of Astrophysics, Cointe-Schlessin, Belgium, 1961
AD 269 914

The energy emitted in the (1,0) band of the Swan system for C_2 , as derived from photoelectric observations, is used to calculate the variation between the density of the C_2 molecule in regions close to the nucleus and that in external regions of the head.

26. P. Swings and J. L. Greenstein
PRESENCE DES RAIES INTERDITES DE L'OXYGEN DANS LES SPECTRA COMETAIRES
Comptes Rendus 246, 511 (1958)

The identification of $\alpha(\text{I})$ in cometary spectra is presented.

27. J. L. Greenstein and C. Arpigny
THE VISUAL REGION OF THE SPECTRUM OF COMET MRKOS (1957d) AT HIGH
RESOLUTION
Astrophysical Journal 135, 892 (1962)

The emission line and band spectrum of the head of Comet 1957d are analyzed and presented in a table of identifications. The C₂ and NH₂ bands produced by resonance fluorescence were nearly completely resolved, while the Na(I) lines were found to be asymmetric with respect to the nucleus.

28. J. L. Greenstein
THE SPECTRUM OF COMET HUMASON (1961e)
Astrophysical Journal 136, 688 (1962)

Spectroscopic observations of Comet 1961e were analyzed and presented in a table of identifications.

29. J. L. Greenstein
HIGH-RESOLUTION SPECTRA OF COMET MRKOS (1957d)
Astrophysical Journal 128, 106 (1958)

A new second-order effect observed in high-dispersion Coude' spectra of Comet Mrkos is presented in a detailed study of Swings' resonance-fluorescence mechanism. Intensity ratios between individual rotational cyanogen lines were found to change within 4000 km on opposite sides of the nucleus and are reportedly caused by motions.

30. P. Swings, C. T. Elvey and H. W. Babcock
THE SPECTRUM OF COMET CUNNINGHAM, 1940c
Astrophysical Journal 94, 320 (1941)

The identification of well-resolved ultraviolet bands due to OH and NH in slit spectrograms of Comet Cunningham is reported along with a description of the observed CH bands, the abundances of the OH and NH molecules, the absence of CN bands in the tail, and bands observed between λ 4000 and 4130.

31. P. Swings et al.
RESEARCH ON RELATIONS BETWEEN COMETARY , SOLAR AND UPPER ATMOSPHERIC
PROCESSES
University of Liege, Department of Astrophysics, Cointe-Schlessin,
Belgium, March 31, 1963
N63-17540

Progress is reported for investigations in time-resolved spectroscopy in the far ultraviolet, the absorption spectra of H₂, D₂, HD, C₃, SO₂¹⁶, SO₂¹⁸, and H₂O, and applicable efforts in instrumentation. The physical mechanisms responsible for cometary phenomena and related space investigations are discussed.

32. L. Remy-Battiau
THE LUMINOSITY VARIATIONS OF COMET HEADS
University of Liege, Department of Astrophysics, Cointe-Schlessin,
Belgium, August 20, 1964
AD 606 655

A study directed toward the elucidation of the relation between solar activity and cometary brightness re-examines Whitney's work on cometary outbursts under the assumption that the light emitted at the time of an outburst is due to scattering of solar radiation by small solid particles. The study considers the masses and required energies and concludes that solar particles are not likely to be responsible for cometary outbursts.

33. B. Donn and H. C. Urey
ON THE MECHANISM OF COMET OUTBURSTS AND THE CHEMICAL COMPOSITION OF COMETS
Astrophysical Journal 123, 339 (1956)

Prominent comet activity is proposed to arise from explosive chemical reactions involving free radical and unstable molecules.

34. B. Donn and H. C. Urey
CHEMICAL HEATING PROCESSES IN ASTRONOMICAL OBJECTS
Mem. Soc. Roy. Sci. Liege, 4^o, 18, 124 (1957)

Chemical heating by recombination of atoms, free radicals, or energetic molecules is considered as an explanation of the cause of comet outbursts.

35. B. Donn
COMETS AND THE CHEMISTRY OF MATTER IN SPACE
Astronomical Journal 64, 126 (1959)

A brief note points out that comets may be looked upon as the initial stages of accumulation from the solar nebula which could have ultimately developed into asteroidal and planetary objects and, thus, that the investigation of comets is a valid approach to cosmic chemistry.

36. B. Donn
FORMATION AND TRAPPING OF FREE RADICALS (A. M. Bass AND H. P. Brodia, editors)
Chap. 11, pp. 347-363, Academic Press, Inc., New York, N. Y., 1960

A brief description of comets is given in a review of the low-temperature chemistry of cometary constituents, comet models, cometary spectra, and postulated mechanisms or causes of cometary phenomena.

37. B. Donn
THE CHARACTERISTICS OF DISTANT COMETS
Ann. d'Astrophys. 25, 319 (1962)

The spectroscopic observations and colors of comets are analyzed and indicate that only sunlight scattered from solid grains can explain the data. The use of previous comet-tail models as set forth by Brandt, Osterbrock, Chamberlain, and Parker to explain interplanetary medium or as a solar-system probe is refuted.

38. H. C. Urey
COMETARY COLLISIONS AND TEKTITES
Nature 197, 228 (1963)

The proposed formation of tektites by cometary collision with the earth is supported.

39. B. Donn
THE ORIGIN AND NATURE OF SOLID PARTICLES IN SPACE
Presented at the New York Academy of Sciences Conference on Cosmic Dust, Goddard Space Flight Center, Greenbelt, Md., November 21-22, 1963

An analysis of the types of particles that exist in interplanetary space is concerned with the collection and detection of such particles and with the identification of their primary source. Possible sources of such material are considered to be primary grains, cometary dust, asteroidal dust, meteorite ablation products, meteoric residue, and interstellar grains.

40. B. Donn and G. W. Sears
PLANETS AND COMETS: ROLE OF CRYSTAL GROWTH IN THEIR FORMATION
Science 140, 1208 (1963)

Crystal growth theory is applied to the formation of smoke particles from the primordial solar nebula to indicate that solid particles with filamentary structures will form and thus facilitate successive aggregation into planets, comets, and asteroids.

41. B. Donn
THE ORIGIN AND STRUCTURE OF ICY COMETARY NUCLEI
Icarus 2, 396 (1963)

The origin and structure of the nuclei is examined within the boundaries of presently accepted models. The analysis considers the distance from the sun, velocity, temperature, cloud of comets, and the formation of planets. The structure of the nuclei is considered in terms of an H₂O ice, density, pressure, and temperature.

42. L. S. Marochnik
THE FORM OF COMETARY ENVELOPES
Sov. Astron. 4, 480 (1960) - Astron. Zh. 37, 508 (1960)

Alfven's hypothesis relating to the interaction between cometary gas and a stream of particles carrying a magnetic field is used to show that the form of a cometary envelope is described by a catenary, in accord with observations. The parabolic relationship flowing from the mechanical theory of cometary forms is only a rough approximation. The transverse motions observed in the tails of comets are accounted for in terms of Alfven waves. The upper limit of the magnetic field is estimated. (Author)

43. L. S. Marochnik
SOME MECHANISMS OF THE RADIO EMISSION OF COMETS
Byul. Komis. po. Kometam i Meteoram Astron. Soveta AN SSSR, No. 5, 21-27 (1961): Ref. Zh., Fizika, No. 1, 49 (1963), Abstract 1Zh294
AD 412 180

An investigation is carried out of the transformation of cometary gas plasma oscillations into radio emission. The effective temperature of the plasma waves and the intensity of the arising radio emission are calculated. The latter corresponds to the observed values. It is shown that the reflection of the solar radio emission by the comet plasma is inessential. The effect of the comet's proper magnetic field is also inessential. (LM)

44. L. S. Marochnik
ON THE PLASMA NATURE OF A COMETS' HEAD
Sov. Astron. 6, 532 (1963) - Astron. Zh. 39, 678 (1962)

The gas in a comet's head is considered to be a plasma with a high degree of ionization. The shape of the comet's head and the origin of the ionization are also treated.

45. L. S. Marochnik
INTERACTION OF SOLAR CORPUSCULAR STREAMS WITH COMETARY ATMOSPHERES
I. SHOCK WAVES IN COMETS
Sov. Astron. 6, 828 (1963) - Astron. Zh. 39, 1067 (1962)

An attempt is made to develop the theory of shock waves in application to comets. The possibility of considering the process of collision of a cometary head with a solar corpuscular stream in terms of magneto-hydrodynamics is shown. The parameters of shock waves originating during this process are computed. The results obtained are used to analyze some phenomena in comets. (Author)

46. L. S. Marochnik
WAVE MOTIONS IN COMET TAILS
Sov. Astron. 7, 218 (1963) - Astron. Zh. 40, 284 (1963)

The causes for wave motions in ionized cometary tails are discussed. It is shown that these motions are related to magnetohydrodynamic waves. The increase in amplitude and wavelength with distance from the head to the tail is accounted for as an increment in the local Alfvén velocity.

47. L. S. Maronchnik
INTERACTION BETWEEN SOLAR CORPUSCULAR STREAMS AND COMETARY ATMOSPHERES.
II. "COLLAPSING" ENVELOPES. RADIO-FREQUENCY EMISSION
Sov. Astron. 7, 384 (1963) - Astron. Zh. 40, 504 (1963)

The collapsing envelopes observed in Comet Morehouse 1908 III and other comets are analyzed and correlated with the occurrence of ionization and radio-frequency emission.

48. L. S. Marochnik
CAUSE OF IONIZATION OF COMETARY MOLECULES
Sov. Astron. 7, 544 (1964) - Astron. Zh. 40, 714 (1963)

In this paper it is shown that the focussing of the magnetic field of the solar corpuscular stream leads to an increase in the concentration of protons in the stream. Even if the corpuscular stream was extremely rarified before collision with the comet, the increase of proton concentration is sufficient for explaining the observed lifetime of parent molecules before ionization by recharging $H^+ + M \rightarrow M^+ + H$ (M = a parent molecule). The focussing of the field to the nucleus also makes it possible to understand the location of ions near the cometary nucleus. (Author)

49. V. I. Cherednichenko
THE DISSOCIATION AND IONIZATION OF COMETARY MOLECULES IN THE PHOTON AND CORPUSCULAR FIELD OF SOLAR RADIATION
Astron. Zh. 36, 254 (1959)

An attempt is made to determine the lifetimes of prechosen cometary molecules under bombardment by photon and corpuscular solar radiation.

50. V. I. Cherednichenko
LIFETIME OF COMETARY ICES IN THE FIELD OF PHOTON AND CORPUSCULAR SOLAR RADIATION
Meteoritika, Akad. Nauk. SSSR, Komitet Meteorit. No. 19, 143-54 (1960)

A more complete description is given for the calculation of the lifetimes of assumed cometary molecules under the influence of photon and corpuscular radiation.

51. Yu. V. Evdokimov
MOTION OF THE JACOBINI-ZINNER COMET FROM 1933 TO 1946
Sov. Astron. 7, 415 (1963) - Astron. Zh. 40, 544 (1963)

The orbital elements of the Jacobini-Zinner comet are computed from observations made of the 1933 and 1939 apparitions and the 1939 and 1946 apparitions.

52. Y. V. Yevdokimov
MASSES OF COMET GIACOBINI-ZINNER AND THE DRACONID METEOR STREAM
Smithsonian Contributions to Astrophysics, Vol. 7, pp. 297-299,
Smithsonian Institution Astrophysical Observatory, Washington, D.C., 1963
N63-16664

The change in the mass and motion of Comet Giacobini-Zinner is assessed and related to the Draconid meteor stream.

53. V. Fessenkov
A NOTE ON THE COMETARY NATURE OF THE TUNGUS METEORITES
Smithsonian Contributions to Astrophysics, Vol. 7, pp. 305-308,
Smithsonian Institution Astrophysical Observatory, Washington, D.C., 1963
N63-16664

The fall of the Tungus meteorite is analyzed with evidence given to support the theory that it was a small comet.

54. S. K. Vsekhsvyatski
THE PROBLEMS ABOUT COMETS AND THE SOLAR SYSTEM
Transactions of the Congress of the All-Union Astronomic-Geodetic
Society, Moscow, 1960, pp. 107-119 (1962)
OTS/SLA 63-19537

The theories for the origin of comets and the mechanism of their formation are reviewed. It is concluded that comets and other small bodies permit an estimation of the amount of matter ejected from planets and thus, the study of comets will allow the history of the planetary system to be elucidated.

55. S. K. Vsekhsvyatski
ABSOLUTE MAGNITUDES OF 1954-1960 COMETS
Sov. Astron. 6, 849 (1963) - Astron. Zh. 39, 1094 (1962)

The absolute magnitudes and photometric parameters of 62 comets observed during 1954-1960 are compiled from available photometric and brightness data.

56. S. K. Vsekhsvyatski
OBSERVATIONS AT KIEV OF COMET SEKI-LINES 1962
Sov. Astron. 7, 133 (1963) - Astron. Zh. 40, 176 (1963)

The brightness of the head of Comet Seki-Lines 1962 covering the entire apparition from April 8 to May 6, 1962 is presented.

57. B. Yu. Levin
THE STRUCTURE OF ICY COMET NUCLEI
Sov. Astron. 6, 593 (1963) - Astron. Zh. 39, 763 (1962)

A hypothesis is proposed that the substances of the icy cometary nuclei are present in the form of separate atoms and molecules embedded in an amorphous noncoherent condensate of different volatile substances, and secondly, that the evaporation of volatile substances from the nucleus leaves a porous matrix, the fragments of which are meteoric particles.

58. V. M. Yuzhakov
REMARKS ON THE MAGNETIC FIELD IN THE TAIL OF THE COMET 1957d
Sov. Astron. 7, 591 (1964) - Astron. Zh. 40, 779 (1963)

The induction of the magnetic field in the tail of the Comet Mrkos 1957d is determined from the helical structure of the field, and the value found was $5 \cdot 10^{-6} \text{G}$, which is less than the interplanetary field by a factor of approximately ten. (Author)

59. D. O. Mokhnach
EFFECT OF PHOTODISSOCIATION ON THE DISTRIBUTION OF SURFACE BRIGHTNESS
IN THE CARBON ATMOSPHERE OF COMETS
Dokl. AN SSSR, Astronomiya, Tom 157, No. 2, 309-312, Izdatel'stvo "Nauka", 1964
ST-OA-10195 (NASA)

An attempt is made to construct a simple model of a carbon coma, considering the deviation in the distribution of surface brightness ($1/r$ and $1/r^2$) as observed in Comet Burnham (1959k).

60. K. A. Shteins and S. Ya. Sture
THE DIFFUSION OF COMETS
Sov. Astron. 6, 398 (1962) - Astron. Zh. 39, 506 (1962)

As Part IV, the problem of new comets is assessed in terms of diffusion processes. The study concludes that the stabilization of the diffusion process involves several million years.

61. E. A. Dibai
ORIGIN OF COMETARY NEBULAE II
Sov. Astron. 7, 606 (1964) - Astron. Zh. 40, 795 (1963)

It is shown that the principal morphological characteristics of cometary nebulae may be represented as the result of focusing of shock waves originating at the interface between a cold, dense neutral gas and an ionized gas in the Stromgren zone. (Author)

62. O. V. Dobrovol'skiy
RADIO EMISSION FROM COMETS
Byul. in-ta Astrofiz. AN Tadzh SSR, No. 26, pp. 3-11 (1958)
AD 264 497

A review of the reported radio emissions observed from comets and the theoretical mechanism or cause of such emission is given.

63. A. D. Dubyago
STRUCTURE OF COMET NUCLEI AND FORMATION OF METEOR STREAMS
Astron. Zh. 27, 5 (1950)
AD 120 694

The structure of comet nuclei is considered as consisting of many separate solid bodies of a quite large size. It is shown that the density of the nuclei can be estimated from the periodic processes observed in comets. The velocity with which meteors leave the comet head is estimated. It is concluded that the meteor swarms associated with periodic comets must originally have a small extent perpendicular to the plane of the orbit, and that the rate of propagation of the swarm may be evaluated.

64. V. G. Fesenkov
ON THE NATURE AND ORIGIN OF COMETS
Sov. Astron. 6, 459 (1963) - Astron. Zh. 39, 583 (1962)

In an attempt to discover the origin of comets, it is postulated that short-period comets are generated from aperiodic comets, that cometary nuclei consist of compact agglomerations of fairly unstable particles, that the total mass of a comet can be estimated from the brightness of the comets head and from reaction effects attendant upon the rotation of the head about the comets axis, and that the distance between the component parts of the nucleus is quite short. In conclusion, it is stated that such compact clusters of unstable species could not possibly originate in volcanic eruptions from the interior of a planet.

65. B. A. Vorontsov-Vel'yaminov
PARTIAL GAS DENSITIES IN COMET 1942g WHIPPLE
Sov. Astron. p. 674 - Astron. Zh. 37, 709 (1960)

The partial gas densities in Comet Whipple are computed from the absolute monochromatic emission spectra of the CN 3883, C₂ 4730, and C₃ 4050 bands as determined by reference to stellar spectra.

66. S. M. Poloskov
THE INFRARED SPECTRUM OF COMETS
ca 1951
N64-23179

A study of the infrared spectra of comets refutes Swings identification of the (red) system of the CN molecule and assigns this emission to $A^2\Pi-2\Sigma$ system of the N_2^+ molecule.

67. S. V. Orlov and S. M. Poloskov
COMETS
?
N64-24654

A summary of Soviet studies of comets covers comet models, cometary physics, and the origin and evolution of comets.

68. L. Biermann
COMET TAILS AND SOLAR CORPUSCULAR RAYS
Zeitschrift fur Astrophysik 28-29, 274 (1950-51)

The acceleration of long comet tails, consisting of CO^+ and other ions, to that which exceeds the gravitational acceleration of the sun is theorized to be produced by the solar corpuscular radiation of the sun.

69. L. Bierman and E. Trefftz
UBER DIE MECHANISMEN DER IONISATION
Zeitschrift fur Astrophysik 59, 1 (1964)

The possible mechanisms for the excitation of the forbidden oxygen lines in comets are discussed along with the production by ionization of suitable parent molecules which can account for the observed emissions of C_2 , CN, and CO^+ .

70. D. Antrack, L. Bierman and Rh. Lust
SOME STATISTICAL PROPERTIES OF COMETS WITH PLASMA TAILS
Annual Review of Astronomy and Astrophysics, Vol. 2, p. 327, Annual Reviews, Inc., Palo Alto, California, 1964

The report surveys the results obtained from the observations of comets in a study of the solar plasma through its effects on the plasma-tail comets.

71. N. T. Bobrovnikoff
PHYSICAL THEORY OF COMETS IN THE LIGHT OF SPECTROSCOPIC DATA
Rev. Mod. Phys. 14, 167 (1942)

A brief summary of the general problems raised by new spectral data is presented in order to point out certain unacceptable physical theories and to outline observational procedure which may serve to provide better understanding of cometary phenomena.

72. N. T. Bobrovnikoff
ON THE SPECTRA OF COMETS
Astrophysical Journal 66, 439 (1927)

The spectra of 22 comets obtained between 1908 and 1927 are analyzed. A correlation is drawn between the heliocentric distance and the type of continuous spectra and between the phase-angle and the type of spectra. Sudden changes in the spectra are discussed and reasons in support of a fluorescence origin of cometary spectra are given.

73. J. A. Bruwer
PHOTOGRAPHIC OBSERVATIONS OF COMETS
Circulars 7, 20 (1963)

The photographic observation of Comets Seki-Lines 1962c, Temple 2, and Humanson 1961e is tabulated, listing date of observation, magnitude, and position.

74. A. J. Cohen
ASTEROID- OR COMET-IMPACT HYPOTHESIS OF TEKTITE ORIGIN: THE MOLDAVITE
STREWN-FIELDS
Tektites, pp. 189-212, The University of Chicago Press, Chicago, Ill.,
1963
N64-114934

Arguments are presented in support of the comet-impact terrestrial origin of tektites.

75. R. Coutrez, J. Hunaerts and A. Koeckelenbergh
RADIO EMISSION FROM COMET 1956h ON 600 MC
Proc. IRE 46, 274 (1958)

An attempt is made to identify the emission as due to a Λ -type doubling of the level $J = 3/2$ for the $2\Pi_{3/2}$ state of the CH molecules.

76. J. Dufay and A. Baranne
LE SPECTRE DE LA COMETE WILSON-HUBBARD (1961d)
Ann d' Astrophys. 25, 301 (1962)

The spectra of Na, NH_2 , C_2 , and CN as recorded photographically is discussed and explained.

77. W. C. Erickson and P. Brissenden
A SEARCH FOR DECAMETRIC RADIATION FROM THE COMET WILSON 1961d
Astrophysical Journal 136, 1138 (1962)

A search for decametric radio emission from Comet Wilson made by Clark Lake radio astronomy station reports definite negative results.

78. F. H. Flynn
INTENSE FAR-RED EMISSION FROM COMET CANDY (1960n)
Observatory 81, 247 (1961)
- The observation of red emission near 7900 and 8100Å is tentatively assigned to CN.
79. C. C. Kiess
RECENT ADVANCES IN ASTRO-GEOPHYSICS
Georgetown College Observatory, Georgetown University, Washington, D. C.,
1964
N64-15286
- A brief lecture presents a general description of comets and the role they play in the study of the formation of the solar system.
80. W. Liller
THE NATURE OF THE GRAINS IN THE TAILS OF COMETS 1956h AND 1957d
Astrophysical Journal 132, 867 (1960)
- Continuous spectra between λ 3400 and λ 6400 obtained from observations of the tails of Comets Arend-Roland (1956h) and Mrkos (1957d) are compared with theoretical light scattering curves. Results indicate that iron spherules of an average diameter of 0.6μ and masses of $8 \times 10^{-13}g$ produced the radiation. Considerations of the brightnesses of the tails allow estimates to be made of the total masses of the particles.
81. W. Liller
PHOTOELECTRIC PHOTOMETRY OF COMETS
Astronomical Journal 66, 372 (1961)
- A description is given of narrow-band photoelectric photometry of Comets Arend-Roland (1956h), Mrkos (1957d), Encke, and Burnham (1959k). The observations are summarized in three parts dealing with head spectra, tail spectra, and monochromatic isophotal contours of Comet Burnham.
82. R. A. Lyttleton
A COMETARY MECHANISM FOR THE FORMATION OF TEKTITES
Proc. Roy. Soc. A 272, 467 (1963)
- The formation of tektites is theorized to be caused by short-period comets which have an eccentricity small enough to allow the accretion of cometary material to occur during the passage of the earth through the comet and thus, produce a narrow jet of material falling vertically downward through the atmosphere.

83. R. A. Lyttleton and J. M. Hammersley
THE LOSS OF LONG-PERIOD COMETS FROM THE SOLAR SYSTEM
Monthly Notices of the Royal Astronomical Society 127, 257 (1964)

The loss of long-period comets from the solar system by planetary action is estimated statistically.

84. B. G. Marsden and G. van Biesbroeck
THE ORBIT OF COMET 1944I (van GENT-PELTIER-DAIMACA)
Astronomical Journal 68, 235 (1963)

A hyperbolic orbit of the Comet 1944I, first observed in 1943 by Gent, is determined from positions covering a 57-day arc.

85. G. van Biesbroeck and B. G. Marsden
ORBIT OF COMET 1954V (ABELL)
Astronomical Journal 68, 212 (1963)

From 34 observations made a year after the comet had attained its perihelion, it is calculated that the hyperbolic excess of the osculating orbit is 19 times its mean error, but that the "original" orbit was elliptical.

86. A. McKellar
SOME TOPICS IN MOLECULAR ASTRONOMY
J. Roy. Astron. Soc. Canada 54, 97 (1960)

Spectroscopic studies of molecules in various astronomical bodies are reviewed.

87. A. McKellar
INTENSITY MEASUREMENTS ON EMISSION BANDS IN COMETARY SPECTRA
Rev. Mod. Phys. 14, 179 (1942)

Intensity measurements on the bands in the spectra of Comet Jurlof-Achmarof-Hassel (1939d) and Comet Cunningham (1940c) are presented in one of the first reports on the quantitative spectrophotometry of comets. The mechanism of the excitation of the CN, C₂, and CH cometary bands is considered in the light of such measurements. The resonance-fluorescence mechanism apparently accounts for the production of CN emission bands.

88. A. McKellar
COMPARISON OF THE λ 3883 CN BAND IN THE SPECTRA OF COMETS 1940c AND 1942g
Astrophysical Journal 100, 69 (1944)

Differences in the structure of the λ 3883 (0,0) CN band as observed in the spectra of Comet Cunningham (1940c) and Comet Whipple-Fedtke-Tevzadze (1942g) are noted and discussed in terms of the resonance production of the bands and the effects of the different heliocentric distances and radical velocities of the comets.

89. A. McKellar
ROTATIONAL DISTRIBUTION OF CH MOLECULES IN THE NUCLEUS OF COMET
CUNNINGHAM (1940c)
Astrophysical Journal 98, 1 (1943)

From the observed profile of the $\lambda 4315$ $^2\Delta$, $^2\Pi$ CH₂ band in the comet, the distribution of the rotational levels of the upper $^2\Delta$ state is found. Assuming the resonance mechanism for the production of the band, the distribution among the rotational levels of the normal $^2\Pi$ state is derived. The results indicate that all the molecules exist in the two lowest rotational levels, $K = 1$ and $K = 2$.

90. F. D. Miller
FILTERS FOR COMET PHOTOGRAPHY
Pub. Astron. Soc. Pac. 70, 279 (1958)

The analysis of several components of the structure of a comet by means of direct photography with suitable emulsion/filter combinations is illustrated with results obtained from the observation of Comet Mrkos 1957d.

91. F. D. Miller
THE TYPE I TAIL OF COMET 1955e
Pub. Astron. Soc. Pac. 74, 60 (1962)

Extended analysis of observations made of Comet Mrkos (1955e) presents two previously unobserved bands of CO⁺ at λ 6189 and 6239 and an unidentified emission near λ 6600. The existence of the comet's well-developed Type-I tail observed at a high heliographic latitude in a period of comparative solar calm is brought forth as noteworthy.

92. F. D. Miller
OBJECTIVE-PRISM SPECTROGRAMS OF COMET HUMANSON (1961e)
Pub. Astron. Soc. Pac. 74, 528 (1962)

Analysis of four objectives-prism spectrograms of Comet Humanson (1961e) is given. Bands of neutral molecules such as CN and C₂ were not found in the spectra. The (1,0), (2,0) and (3,0) CO⁺ tail bands appeared superimposed on a continuum.

93. F. D. Miller
NOTE OF THE SPECTRUM OF COMET IKEYA (1963a)
Astrophysical Journal 139, 766 (1964)

Unidentified emission at λ 6158, 6199, 6542, and 6562 observed in the spectra of Comet Ikeya (1963a) is reported and postulated to be due to ions.

94. M. F. Walker
OBSERVATIONS OF COMETS BAKHAREV-MacFARLAND-KRIENKE, 1955f, AND BAADE, 1954h
Pub. Astron. Soc. Pac. 70, 191 (1958)

The results of three-color photoelectric observations obtained in 1955 at the Mount Wilson and Palomar Observatories are reported.

95. F. L. Whipple
A COMET MODEL. I. THE ACCELERATION OF COMET ENCKE
Astrophysical Journal 111, 375 (1950)

A comet model is proposed, in which the nucleus is visualized as a conglomerate of ices, "volatiles", and meteoric materials combined at extremely low temperatures. The model resolves the chief problems of cometary motions and accounts for a number of other cometary phenomena.

96. F. L. Whipple
A COMET MODEL. II. PHYSICAL RELATIONS FOR COMETS AND METEORS
Astrophysical Journal 113, 464 (1951)

The loss of gaseous and meteoric materials from the nucleus is considered in terms of the comet's structure and compared with previous observations.

97. F. L. Whipple
A COMET MODEL. III. THE ZODIACAL LIGHT
Astrophysical Journal 121, 750 (1955)

An attempt is made to explain the occurrence of the zodiacal light, which arises from the scattering and diffraction of sunlight by small particles, by the postulation of a comet model which can account for the replenishment of these particles by ejection or disintegration by comets.

98. F. L. Whipple
PROBLEMS OF THE COMETARY NUCLEUS
Astronomical Journal 66, 375 (1961)

The icy model is examined critically through a presentation of the relevant observational and theoretical evidence of its existence and nature.

99. F. L. Whipple
REMARKS ON COMETS, METEORS, AND PLANETARY EVOLUTION
Smithsonian Astrophysical Observatory, Harvard College Observatory,
Cambridge, Mass.
N64-24771

A discussion of comet accumulation in the outer parts of the solar system is presented.

100. C. Whitney
COMET OUTBURSTS
Astrophysical Journal 122, 190 (1955)

Several comet outbursts accompanied by the ejection of spherical halos are investigated. Special attention is paid to the mass and energy ejected in a typical halo. On the basis of the results, it is suggested that the energy of an outburst may be derived from normal isolation. The activity can possibly be explained in terms of the icy-conglomerate comet nucleus. (Author)

101. A. A. Wyller
C₂ PHILLIPS BANDS IN EMISSION FROM COMET CANDY (1960n)
Observatory 82, 73-5 (1962)

It is suggested that the λ 7906 and λ 8106 emission observed from Comet Candy may be due to the infrared C₂ Phillips system ($l_{\pi_u} = l_{\sigma_g}^+$).

102. H. Zanstra
THE EXCITATION OF LINE AND BAND SPECTRA IN COMETS BY SUNLIGHT
Monthly Notices of the Royal Astronomical Society 89, 178 (1928)

The line and band spectra observed in the head of a comet are theorized to be produced by the absorption of sunlight and subsequent resonance or fluorescence re-emission.

103. COMETARY TAILS
Defense Documentation Center, Cameron Station, Alexandria, Va., July 1962
ARB No. 10857

A bibliography of 29 reports dealing with observational and laboratory investigations of comets is offered.

104. H. Alfven
ON THE THEORY OF COMET TAILS
Tellus IX, 92 (1957)

It is shown that some of the difficulties of Biermann's theory, which postulates that the repulsive force in comet tails is due to a corpuscular radiation from the sun, can be overcome if the assumed radiation consists of beams with a frozen-in magnetic field of the same type as required in the electric field theory of magnetic storms and aurorae. The interaction of such a beam with the head of a comet could produce an amplified magnetic field which determines the shape of the tail. The high accelerations observed in tails may be due to electromagnetic forces.

105. D. B. Beard and M. P. Nakada
INTERPLANETARY MAGNETIC FIELDS AS A CAUSE OF COMET TAILS
Nature 199, 580 (1963)

In explanation of the formation of cometary tails, it is pointed out that the gases in cometary comae can be efficiently ionized by a solar wind of ionized hydrogen embedded in a magnetic field, and that an interplanetary magnetic field can couple the cometary gas to the solar wind.

106. T. Carrington
FLUORESCENCE IN COMETS AS A MARKOV PROCESS
Astrophysical Journal 135, 883 (1962)

The fluorescence mechanism for the emission of electronic spectra of diatomic radicals in comet heads, as proposed by Swings and Hunaerts, is treated statistically and compared with previous less-rigorous calculations.

107. F. Hoyle and M. Harwit
PLASMA DYNAMICS IN COMETS. I. PLASMA INSTABILITY
Astrophysical Journal 135, 867 (1962)

An attempt is made to find a mechanism consistent with Bierman's theory that tail ions are accelerated through interaction with streams of solar particles. The field-free case is examined in an effort to establish conditions for which cometary plasma acceleration may be enhanced by plasma instability. From this it is concluded that plasma instability does not appreciably contribute to tail plasma acceleration.

108. M. Harwit and F. Hoyle
PLASMA DYNAMICS IN COMETS. II. INFLUENCE OF MAGNETIC FIELDS
Astrophysical Journal 135, 875 (1962)

In an attempt to find a mechanism consistent with Bierman's theory, it is shown that, if predominantly transverse magnetic fields are imbedded in the solar stream, the observed accelerations can be readily imparted to tail ions. The 10 km sec^{-1} ejection velocities from comet heads and the filamentary structure of many comet features are accounted for. Observational tests for the transverse field hypothesis are suggested.

109. C. R. O'Dell
EMISSION-BAND AND CONTINUUM PHOTOMETRY OF COMET BURNHAM, 1959k
Pub. Astron. Soc. Pac. 73, 35 (1961)

Two interference filters were used to observe the continuum around $\lambda 4470$ and the C_2 Swan band sequence near $\lambda 4700$. The data obtained includes information on the variation of surface brightness with distance from the nucleus, on changes in the comet with time and heliocentric distance, and the distribution of the material responsible for the band or continuum emission.

110. D. E. Osterbrock
A STUDY OF TWO COMET TAILS
Astrophysical Journal 128, 95 (1958)

Photographic observations of the directions of the tails of Comet Baade (1954h) and Comet Haro-Chavero (1954k) indicate that the tail lies in the orbital plane roughly midway between the radial and tangential directions. Analysis of the observations indicate that the material in the tail must be subjected to a resisting force roughly equal to the radial repulsive force of the sun, that this resisting force can be caused by the interplanetary gas if the tail contains a large fraction of hydride molecules, and that the possibility the tail consists of solid particles small in comparison with the wavelength of light cannot be ruled out.

111. C. R. O'Dell and D. E. Osterbrock
EMISSION-BAND AND CONTINUUM PHOTOMETRY OF COMET SEKI (1961f)
Astrophysical Journal 136, 559 (1962)

C₂ densities are obtained from photoelectric measurements of the continuum and C₂ emission-band fluxes from Comet Seki (1961f) and Comet Burnham (1959k).

112. J. A. O'Keefe and B. N. Shute
ORIGIN OF TEKTITES
Science 139, 1288 (1963)

It is shown from the observed distribution of tektites that they cannot be the result of cometary or meteoritic impact but, rather, can be accounted for as a result of fusion stripping of a satellite.

113. E. J. Öpik
PHOTOMETRY, DIMENSION, AND ABLATION RATE OF COMETS
The Irish Astronomical Journal 6, 93 (1963)

Considering the peculiarities of light distribution in the coma, it is estimated that the brightness of comets varies inversely as the first power of distance from the observer instead of the traditionally-used second power. This is postulated to be of major importance for artificial comets, making their construction prohibitive. The sudden appearance of radicals and ions in cometary envelopes is said to point to an active shell or radiation belt surrounding the nucleus. Formulae for absolute magnitudes and photometric radii of comets are given and confirmed by recoil radii. These are seen to be much smaller than the dimensions of "false nuclei" observed telescopically. The total evaporation rate of the nuclear ices is estimated, and the luminescent radicals (C₂, CN) and ions (CO⁺) are reported to account for almost one percent of the total gaseous mass. The layered mechanism of simultaneous evaporation of constituents of different volatility is discussed.

From molecular weight and cosmogonic considerations, it is theorized that solid hydrogen is an important constituent of the nuclei. The mechanism of outbursts is said to be a sudden increase of the evaporation area caused by shake-off of clouds or fragments. The revision of the photometric parameters of comets, based on new formulae, is suggested.

114. E. J. Öpik
SURVIVAL OF COMET NUCLEI AND THE ASTEROIDS
University of Maryland Mimeo, 59 pp., 1961

The article considers the dynamic survival of comets and other stray bodies in encounters with planets in an effort to uncover by statistics any possible genetic link between comets and asteroids.

115. E. J. Öpik
NOTE ON STELLAR PERTURBATIONS OF NEARLY PARABOLIC ORBITS
Proc. Amer. Acad. Arts and Sciences 67, 169 (1932)

The effect of passing stars on the stability of the orbits of meteors and comets in the solar system is assessed in a statistical consideration.

116. E. J. Öpik
THE SPIKE OF COMET AREND-ROLAND 1956h
The Irish Astronomical Journal 5, 37-50 (1958)

The spike of Comet Arend-Roland is discussed and interpreted to be a "synchro" consisting of dust particles of different radii released in an outburst which left the nucleus instantaneously devoid of all volatile material.

117. E. J. Öpik
THE MOTION OF THE CONDENSATION IN THE TAIL OF HALLEY'S COMET JUNE 5-8, 1910
Zeitschrift für Astrophysik 58, 192 (1964)

The observed motions of the condensation in Halley's comet are found to agree with that of hypothetical rays calculated from the observed behavior of rays in Type-I plasma tails. It is suggested that this analogy may offer a clue to the understanding of the evolution and metamorphosis of the observed ray emission in comet tails.

118. D. H. Robey
A NEW MODEL FOR COMETS--THE COLD, PARTIALLY CONDENSED, MAGNETIZED PLASMA
J. Astronautical Sciences 9, 41 (1962)

A study of the general properties of comets presents those characteristics which suggest that a comet's nucleus may be surrounded by and attached to

a magnetized plasma. This theory is used to postulate a formula for coma contraction and is also applied to comet outbursts. The contraction is believed to be caused by the solar wind which may, during periods of solar flare, cause a sudden contraction to effect a comet outburst.

119. G. J. Szasz and S. F. Singer
SYMPOSIUM ON THE PHYSICS OF COMETS AND METEORS
Office of Naval Research, London, November 18, 1952
AD 382

An account of a recent Liege symposium includes discussions of the spectroscopy of comets, the structure of the head and tail, and the origin and evolution of comets.

120. K. Wurm
THE ULTRAVIOLET SOLAR SPECTRUM AND COMETS
Proceedings of the Tenth International Astrophysical Symposium, Liege, July 11-14, 1960
AD 269 781

The importance of the interaction of solar ultraviolet radiation with cometary atmospheres is assessed, concluding that its action may be weak in comparison with the role of corpuscular radiation.

121. K. Wurm
STRUCTURE AND DEVELOPMENT OF COMETARY TAIL
Hamburger Sternwarte, Hamburg-Bergedorf, Germany, March 31, 1964
AD 602 048

A final report on contract AF61(052)-583 presents five separate papers which deal with the study of the structure and development of ion-type cometary tails.

122. K. Wurm
DIE IONISIERUNG IN DEN KOMETEN
Icarus 1, 144 (1962)

New support is given to the theory that the ionization of cometary molecules is intrinsic to the cometary atmospheres themselves. It is argued that the ionization occurs in a limited region in front of the nucleus and that the ions are expelled in narrow rays within a small cone which is directed toward the sun. Apparently, outbursts lead to the formation of a shrinking parabolic envelope around the nucleus, which is accompanied by a closing-in of the tail rays to the tail axis. The true mechanism of ionization is still obscure.

123. K. Wurm and B. Balazs
THE HEADS OF COMETS AND THE LIFETIMES OF THEIR MOLECULES
Icarus 2, 334 (1963)

From the extension and spherical shape of the CN and C₂ heads, an average lifetime of these molecules until ionization of the order 10⁶ seconds for unit heliocentric distance is derived. This long lifetime excludes densities of protons in the "solar wind", which exceed $n_p = 10 \text{ cm}^{-3}$. (Author)

124. K. Wurm
BRIGHTNESS AND STRUCTURE OF THE NA-EMISSION IN COMETS
Hamburger Sternwarte, Hamburg-Bergedorf, Germany, March 31, 1964
AD 604 048

The structure of a Na-coma is investigated. In consequence of a relatively high repulsive force originating from light pressure and a relatively high average lifetime of the atoms, a typical parabolic shape to the coma is expected.

125. A. Mammano and K. Wurm
THE AXES OF THE TYPE-I TAILS OF COMETS
Hamburger Sternwarte, Hamburg-Bergedorf, Germany, March 31, 1964
AD 604 048

The axes of the Type-I tails of comets are defined by the directions (position angles at the nucleus) to which the tail rays are "closing in." The axes are always lagging behind the prolonged radius vector. It is shown that the directions of the tail axes are determined by the forces which regulate the outflow of the tail material from its source in the head. A direct influence of the "solar wind" on the position of the tail axes is not apparent. (Author)

126. K. Wurm
AN EXPANDING HALO OF COMET ALCOCK (1963b)
Hamburger Sternwarte, Hamburg-Bergedorf, Germany, March 31, 1964
AD 604 048

On May 27/28, 1963 Comet Alcock showed an increase in light of about three magnitudes accompanied by an outbreak of gas and dust. The gas halo expanded with a velocity of one kilometer per second. The expansion of the dust material was much smaller amounting only to 50 to 100 meters per second. (Author)

127. M. J. S. Belton, J. C. Brandt and P. W. Hodge
ON THE CHARACTERISTICS OF DISTANT COMETS
Space Science Laboratory, University of California, Berkeley, California
AD 299 839

Donn's article on the characteristics of distant comets is criticized. It is shown that his arguments concerning the composition of the tails and their curvature and orientation are mutually contradictory. Brandt's use of these tails to probe the interplanetary medium is strengthened and his arguments for a transition region between the solar wind and the solar breeze at 2 AU are reinforced.

128. J. C. Brandt
ON THE STUDY OF COMET TAILS AND MODELS OF THE INTERPLANETARY MEDIUM
Astrophysical Journal 133, 1091 (1961)

The theories of Bierman, Parker, and Chamberlain are applied to Osterbrock's observations of Comets Baade 1954h and Haro-Chavira 1954k.

129. J. C. Brandt
INTERPLANETARY MEDIUM PHYSICS AND COMET TAILS
California University, Berkeley, 1964
AD 603 780

The programs, results, and reports resulting from research on interplanetary medium physics and comet tails are summarized.

130. S. Grundzinska
THE ABUNDANCE OF CO^+ IONS IN THE TAILS OF COMETS
Ann. d'Astroph. 23, 797 (1960)

The abundance of CO^+ in the tail of Comet Bester (1947k) is found to be 30 to 40 times greater than that of CN in the head. Assuming that the abundance for CN is taken equal to that suggested for C_2 by Wurm, the abundance of CO^+ ions in the tail around the region of the head is estimated to be on the order of 10^6 per cm^3 .

131. S. L. Miller
THE OCCURRENCE OF GAS HYDRATES IN THE SOLAR SYSTEM
Proc. Nat. Acad. Sci. 47, 1798 (1961)

The occurrence and properties of the hydrates in planetary, interplanetary, and cometary environment is discussed. A mixed hydrate of methane, carbon dioxide, ethane, etc. is postulated to be a likely constituent of comets.

132. K. Watson, B. C. Murray and H. Brown
THE STABILITY OF VOLATILES IN THE SOLAR SYSTEM
Icarus 1, 317 (1963)

A study of the stability of the ices of water, ammonia, carbon dioxide, and methane is extended to the rings of Saturn, the surfaces of the smaller satellites of Jupiter and Saturn, and bodies in orbits similar to those of short-period comets.

133. D. E. Blackwell and R. V. Willstrop
A STUDY OF THE MONOCHROMATIC POLARIZATION OF COMET AREND-ROLAND (1956h)
Monthly Notices of the Royal Astronomical Society 117, 590 (1957)

Polarization measurements obtained with glass and gelatin filters are reported to have isolated the continuum near 4530\AA and the (0,0) CN emission band near 3850\AA . The polarization curve of the continuum was found to agree reasonably with that of a metallic meteorite, and the amount of polarization in the CN measurements was consistent with a fluorescence mechanism.

134. J. D. Kraus
OBSERVATIONS AT A WAVELENGTH OF 11 METERS DURING THE CLOSE APPROACH OF COMET AREND-ROLAND
Astronomical Journal 53, 55 (1958)

The observation of a radio source which may have been related to Comet Arend-Roland is reported.

135. J. W. Shaw
NATURAL ENVIRONMENT OF INTERPLANETARY SPACE
The Ohio State University Research Foundation, Columbus, Ohio, 1960
AD 250 230

Chapter IV of this report is devoted to solid particles in interplanetary space and includes a short description of the form and composition of comets, their orbits, and the number of observed and unobserved comets.

LABORATORY STUDIES

136. G. Herzberg, A. Monfils and B. Rosen
MOLECULAR SPECTRA IN THE REMOTE ULTRAVIOLET. INDUCTORY REPORT
Mem. Soc. Roy. Sci. Liege 4, 146 (1961)
OTS/SLA 63-10245

Recent progress made in vacuum ultraviolet spectroscopy is reviewed as it applies to astrophysics and theoretical molecular spectroscopy. Individual molecular spectra of the gaseous state and recent improvements in vacuum spectrographs are discussed.

137. G. Herzberg
RECENT LABORATORY INVESTIGATIONS OF MOLECULES OF ASTRONOMICAL INTEREST
Mem. Soc. Roy. Sci. Liege 28, 397 (1956)
AD 132 241

Laboratory investigations of molecules of importance to stellar atmospheres, planetary atmospheres, and comets are summarized. The discussion includes the SiC₂ molecule in carbon stars, possible detection of polyatomic molecules in stellar atmospheres, the dissociation of diatomic molecules, methods for band spectroscopy to determine temperature, the mechanism of OH production in the upper atmosphere, molecular hydrogen in planetary atmospheres, and the formation of molecules in comets.

138. G. Herzberg
LABORATORY INVESTIGATIONS OF THE SPECTRA OF INTERSTELLAR AND COMETARY MOLECULES
Mem. Soc. Roy. Sci. Liege, Ser. 4, 15, 291 (1955)

The identification and formation of diatomic molecules in interstellar, planetary, and cometary medium is summarized. Laboratory data are presented for CN⁺ and NH⁺ and for the triatomic radicals C₃ and NH₂ of comets. The possible presence of HCO in interstellar medium and planetary atmospheres is discussed.

139. J. Oro
COMETS AND THE FORMATION OF BIOCHEMICAL COMPOUNDS ON THE PRIMITIVE EARTH
Nature 190, 389 (1961)

It is suggested that one important consequence of the interactions of comets with the earth is the accumulation of relatively large amounts of carbon compounds which are known to be transformed spontaneously into amino acids, purines, and other biochemical compounds. Laboratory experiments are described in verification of this theory.

140. A. E. Potter and B. Del Duca
LIFETIME IN SPACE OF POSSIBLE PARENT MOLECULES OF COMETARY RADICALS
Icarus 3, 103 (1964)

The space lifetimes of some possible parent molecules of radicals are estimated from laboratory measurements of absorption cross sections and the solar ultraviolet flux. The parent molecules include ethylene, acetylene, methane, cyanogen, hydrazine, ammonia, water, etc.

141. P. Wilkinson
DIATOMIC MOLECULES OF ASTROPHYSICAL INTEREST: IONIZATION POTENTIALS AND DISSOCIATION ENERGIES
Astrophysical Journal 138, 778 (1963)

A critical analysis is made of the ionization potentials and dissociation energies of 148 diatomic molecules and molecular ions of astrophysical importance. The data is summarized in a table and includes values and references for C_2 , CH, CN, CO^+ , NH, N_2^+ , OH^+ , O_2^+ , as well as others.

142. G. J. Pontrelli
THE FORMATION AND PROPERTIES OF CERTAIN COMETARY SPECIES
Final Report on NASA Contract NASw 707, E. I. DuPont de Nemours and Company, Wilmington, Delaware, January 1965

C_2 , C_3 , and CH radical-radical reactions and properties observed in the continuous and flash photolysis of diacetylene are related to the postulated mechanisms of radical formation at or near the nucleus of comets.

143. G. Herzberg
THE SPECTRA AND STRUCTURES OF FREE METHYL AND FREE METHYLENE RADICALS
Proc. Roy. Soc. A 262, 291 (1961)

Vacuum ultraviolet photolysis of dimethyl mercury and diazomethane is reported to produce the spectra of the two astrophysically important radicals, CH_3 and CH_2 . Analysis of the spectra results in the determination of the electronic and geometric structure of the radicals, which can be applied to future analysis of cometary spectra.

144. G. Herzberg and J. Shoosmith
ABSORPTION SPECTRUM OF FREE CH_3 AND CD_3 RADICALS
Can. J. Phys. 34, 523 (1956)

A preliminary study presents the absorption spectrum of CH_3 as produced by the vacuum ultraviolet flash photolysis of dimethyl mercury.

145. G. Herzberg and P. A. Warsop
SPECTRUM AND STRUCTURE OF THE FREE HNCN RADICAL
Can. J. Phys. 41, 286 (1963)

The spectra and structure of HNCN produced in the flash photolysis of diazomethane is investigated. The 3440\AA band is assigned to this free radical, and its ground and first-excited state are determined.

146. G. Herzberg
LABORATORY PRODUCTION OF THE λ 4050 GROUP OCCURRING IN COMETARY SPECTRA: FURTHER EVIDENCE FOR THE PRESENCE OF CH_2 MOLECULES IN COMETS
Astrophysical Journal 96, 314 (1942)

The λ 4050 system occurring in cometary spectra is assigned to CH_3 (which is later refuted by Herzberg and others and assigned to C_2).

147. G. Herzberg and J. Shoosmith
SPECTRUM AND STRUCTURE OF THE FREE METHYLENE RADICAL
Nature 183, 1801 (1959)

An explanation for the previous misidentification of the λ 4050 as due to CH_2 is presented through more recent identification of the vacuum ultraviolet spectrum (λ 1400) of CH_2 produced by the photolysis of diazomethane.

148. G. W. Robinson and M. McCarty
THE PRODUCTION AND SUBSEQUENT PHOTOLYSIS OF TRANSIENT PRODUCTS FROM THE PHOTODECOMPOSITION OF DIAZOMETHANE AT 4.2°K
J. Am. Chem. Soc. 82, 1859 (1960)

Experiments on the photolysis of solid diazomethane and its isotopic modifications present evidence for the assignment of part of the observed spectra to an electronic transition of methylene in the near ultraviolet. Other products of the photolysis were trapped, and their nature is described.

149. N. Sreedhara Murthy
A LABORATORY STUDY OF THE 'ROTATIONAL TEMPERATURE' OF CH^+ ($^1\Pi - ^1\Sigma$) COMETARY BAND
Proc. Phys. Soc. 81, 1141 (1963)

The determination of the intensities of five rotational lines of the (0,0) band of the CH^+ ($^1\Pi - ^1\Sigma$) cometary system is reported as the result of an analysis of spectra produced through excitation by a high-frequency electrodeless discharge.

150. A. E. Douglas
LABORATORY STUDIES OF THE λ 4050 GROUP OF COMETARY SPECTRA
Astrophysical Journal 114, 466 (1951)

Study of the spectra obtained from laboratory production of the λ 4050 group previously observed in cometary spectra indicates that it is due to the C_3 molecule. Isotope effects and the fine structure show that hydrogen is not present and therefore, the emission cannot be due to CH_2 as postulated by Herzberg.

151. R. G. Bennett and F. W. Dalby
EXPERIMENTAL OSCILLATOR STRENGTHS OF CH AND NH
J. Chem. Phys. 32, 1716 (1960)

The oscillator strengths of the $A^2\Delta$ and $B^2\Sigma$ states of CH and the $A^2\Pi$ state of NH are calculated from the determination of the radiative life-times of the emitting species as produced by electron bombardment of methane and ammonia.

152. K. Clusius and A. E. Douglas
The λ 4050 BANDS OF THE C_3^{13} MOLECULE
Can. J. Phys. 32, 312 (1954)

Excitation of the λ 4050 cometary bands with C_3^{13} provide very good evidence that the C_3 molecule is responsible for this emission in comets.

153. G. V. Marr and R. W. Nicholls
THE EMISSION OF THE ' λ 4050' BANDS AND AN ASSOCIATED VIOLET CONTINUUM IN OXYACETYLENE FLAMES
Can. J. Phys. 33, 394 (1955)

A strong violet continuum is reported to appear with the C_3 bands excited in the luminous region of a fuel-rich oxyacetylene flame. Preliminary photographic intensity measurements on the spectra of the different regions of the flame show strong correlation between the C_3 bands and the continuum.

154. G. V. Marr
COMBUSTION STUDIES OF ASTROPHYSICAL SIGNIFICANCE. III.
The University of Western Ontario, London, Ontario, Canada, March 1, 1957
AD 152 611

Spectroscopic investigation of the luminous mantle of fuel-rich oxyacetylene flames encompasses band-head intensity measurements for the radicals C_2 , CH, C_3 , and CN; rotational plots for C_2 , CH, and OH; and determination of vibrational temperatures and the mechanisms of product formation. The experimental observations of C_3 are considered in relation to previous laboratory and astrophysical investigations. The formation of C_3 in comets is discussed, and the fluorescence mechanism by solar radiation is shown to account for the cometary band emission occurring in the absence of continuum emission.

155. P. S. Skell and L. D. Wescott
CHEMICAL PROPERTIES OF C_3 , A DICARBENE
J. Am. Chem. Soc. 85, 1023 (1963)

The chemical reactions of carbon vapor, produced in vacuo, with olefins at liquid-nitrogen cooled surfaces are reported. The conditions of reaction have been controlled to simulate cometary ambient conditions.

156. B. Rosen
NEW INVESTIGATIONS ON THE C_3 SPECTRUM AT 4050\AA
Astronomical Journal 66, 383 (1961)

A brief summary of laboratory investigation of the λ 4050 system for C_3 and its importance to cometary physics is given.

157. G. V. Marr
COMBUSTION STUDIES OF ASTROPHYSICAL SIGNIFICANCE. 1. A SURVEY OF THE GENERAL MECHANICS OF FLAME PROPAGATION, AND OF RELEVANT EXPERIMENTAL TECHNIQUES
The University of Western Ontario, London, Ontario, Canada, May 1, 1956
AD 101 687

The general mechanics and experimental techniques for flame propagation are presented and directed toward an effort to provide information on excitation conditions in astrophysical sources. Hydrocarbon/oxygen premixed flames are considered and it is suggested that C_2H_2/O_2 flame be used as a source of the C_3 radical which occurs in cool stars and comets.

158. G. Herzberg and D. A. Ramsay
ABSORPTION SPECTRUM OF FREE NH_2 RADICALS
J. Chem. Phys. 20, 347 (1952)

The α -bands observed in comets is assigned to NH_2 through preliminary investigations of the absorption spectra produced in the flash photolysis of NH_3 .

159. G. Herzberg and D. A. Ramsay
THE ABSORPTION SPECTRUM OF FREE NH_2 RADICALS
Discussions of the Faraday Society 14, 11 (1953)

A thorough laboratory investigation of the absorption spectra of NH_2 as produced from the flash photolysis of NH_3 , is presented. The structure of the spectrum and isotope shifts obtained with deuterated NH_3 confirm that NH_2 is responsible for the α -bands observed in cometary spectra.

160. D. A. Ramsay
THE ABSORPTION SPECTRA OF FREE NH AND NH₂ RADICALS PRODUCED BY THE FLASH
PHOTOLYSIS OF HYDRAZINE
J. Phys. Chem. 57, 415 (1953)

Some preliminary results from the flash photolysis of hydrazine includes the determination of the critical flash intensity above which thermal explosion occurs and the observation of the absorption spectra of the NH and NH₂ products of the explosion reaction.

161. D. A. Ramsay
ELECTRONIC SPECTRUM AND STRUCTURE OF THE FREE NH₂ RADICAL
J. Chem. Phys. 25, 188 (1956)

Rotational and vibrational analysis of the NH₂ bands, produced by the flash photolysis of ammonia and hydrazine, is reported to verify the assignment of the α -bands of ammonia to the NH₂ radical.

162. M. W. Feast
AN EMISSION BAND SYSTEM ATTRIBUTED TO THE MOLECULE NH⁺
Astrophysical Journal 111, 344 (1951)

Emission bands produced from the excitation of flowing ammonia in a hollow-cathode discharge tube are identified as NH⁺. The postulated importance of this molecule is based on previous observations of NH in cometary spectra and the dual presence of both CH and CH⁺ in cometary spectra.

163. J. A. Glasel
STABILIZATION OF NH IN HYDROCARBON MATRICES AND ITS RELATION TO COMETARY
PHENOMENA
Proc. Nat. Acad. Sci. 47, 174 (1961)

The ultraviolet spectra of NH resulting from RF discharge through the low-temperature solids CH₄-N₂-A, CH₄-N₂, and NH₃-A is shown in an attempt to substantiate that free radicals such as NH can be trapped in the frozen solids which exist in comets.

164. F. O. Rice and M. Frearno
THE FORMATION OF THE IMINE RADICAL IN THE ELECTRICAL DISCHARGE
J. Am. Chem. Soc. 75, 548 (1953)

The formation of the NH radical from electrical discharge in hydrazoic acid is described. Allied experiments with electrical discharge in ammonia, hydrazine, cyanic acid, and nitrogen-hydrogen mixtures failed to produce the radical.

165. L. J. Stief and V. J. DeCarlo
 ORIGIN OF $\text{NH}(A^3\Pi)$ $\text{NH}(X^3\Sigma^-)$ EMISSION IN COMETS
 Nature 205, 889 (1965)

The photolysis of hydrazine at the krypton resonance lines and at low pressures is reported to produce the λ 3360 emission spectra of NH. The spectra is that of the triplet system which has been previously observed in cometary spectra. From this, hydrazine-type compounds are postulated to be responsible for the NH emission in comets.

166. H. Schuler and A. Michel
 ON NEW EMISSION BANDS FROM ELECTRIC EXCITATION OF AMMONIA
 Z. Naturforsch. 10a, 1 (1955)

Two band systems appearing between 5200 and 8500 \AA are reported to occur upon electrical excitation of NH_3 at one atmosphere.

167. W. Groth and K. H. Welge
 BLITZLICHT PHOTOLYSE UND PHOTOCHEMISCHE ZERSETZUNG DES AMMONIAKS
 Bull. Soc. Chim. Belg. 71, 705 (1962)

The ultraviolet flash photolysis of NH_3 to produce the NH and NH_2 radicals is described.

168. K. D. Bayes, K. H. Becker and K. H. Welge
 FLASH PHOTOLYSIS OF NH_3 IN THE VACUUM ULTRAVIOLET
 Z. Naturforsch. 17a, 676 (1962)

The production of NH_2 and NH radicals from the vacuum ultraviolet photolysis of gas-phase NH_3 at wavelengths between 2200 and 1650 \AA is reported.

169. K. H. Becker, F. Stuhl and K. H. Welge
 FLASH PHOTOLYSIS AND FLUORESCENCE OF NH_3 IN THE VACUUM ULTRAVIOLET
 Bonn University, Germany, 1962
 AD 438 411

The production, kinetics, and electronic stages of the NH_2 and NH radical in the vacuum ultraviolet flash photolysis of NH_3 is described. In fluorescence studies of the primary product NH, the $c^1\Pi$ $a^1\Sigma$ transition, is observed, but not the 3Π $3\Sigma^-$ transition.

170. H. J. Rommel
 PHOTOLYSIS OF AMMONIA IN THE FAR ULTRAVIOLET
 Bonn University, Germany, 1963
 AD 438 494

The influence of the NH radical on the overall mechanism of the ammonia photolysis is assessed.

171. F. Stuhl and K. H. Welge
FLASH PHOTOLYSIS OF NH_3 IN THE VACUUM ULTRAVIOLET. II.
Z. Naturforsch. 18a, 900 (1963)

An analysis is made of the formation of NH in the vacuum ultraviolet photolysis of NH_3 . It is reported that NH radicals appear directly in the $3 \Sigma^-$ state.

172. W. E. Groth
PHOTOCHEMICAL INVESTIGATIONS IN THE FAR ULTRAVIOLET
Bonn University, Germany, 1963
AD 416 366

The report summarizes present progress made in a series of investigations on the far ultraviolet photochemical behavior of NH_3 .

173. W. Groth, H. Okabe and H. J. Rommel
PRIMARY PROCESSES OF NH_3 PHOTOLYSIS AT 1470\AA
Z. Naturforsch. 19a, 507 (1964)

The photolysis of NH_3 at 1470\AA is investigated and found to proceed to 12 percent by reaction to NH radicals and to 88 percent by reaction to NH_2 radicals.

174. K. H. Becker and K. H. Welge
THE INVESTIGATION OF THE FLUORESCENCE AND PHOTOCHEMICAL PRIMARY PROCESSES IN THE VACUUM UV BY NH_3 , N_2H_4 , PH_3 AND THE REACTIONS OF THE ELECTRONICALLY EXCITED RADICALS $\text{NH}^* ({}^1\pi)$, $\text{NH}^* ({}^3\pi)$, $\text{PH}^* ({}^3\pi)$
Z. Naturforsch. 19a, 1006 (1964)

(In German)

175. E. Fink and K. H. Welge
LIFETIME OF THE ELECTRONIC STATES $\text{N}_2(\text{C}^3 \pi_u)$, $\text{N}_2^+(\text{B}^2 \Sigma^+ u)$, $\text{NH}(\text{A}^3 \pi)$, $\text{NH}(\text{c}^1 \pi)$,
Z. Naturforsch. 19a, 1193 (1964)

(In German)

176. K. D. Beyer and K. H. Welge
PHOTODISSOCIATION OF H_2 , N_2 , O_2 , NO, CO, H_2O , CO_2 and NH_3 IN EXTREME VACUUM ULTRAVIOLET
Z. Naturforsch. 19a, 19-28 (1964)

(In German)

177. K. H. Becker and K. H. Welge
 FLUORESCENCE OF NH RADICALS DURING THE PHOTODISSOCIATION OF NH_3 IN THE
 VACUUM ULTRAVIOLET
 Z. Naturforsch 18a, 600-3 (1963)
 (In German)
178. A. E. Douglas and P. M. Routly
 THE SPECTRUM OF THE CN^+ MOLECULE
 Astrophysical Journal 119, 303 (1954)
 It is reported that two band systems due to two $^1\Sigma - ^1\Sigma$ rotational
 transitions of the astrophysically-important CN^+ molecule have been
 produced from a discharge through helium mixed with a trace of C N_2 .
 Four other unidentified bands are also reported.
179. R. G. Bennett and F. W. Dalby
 EXPERIMENTAL OSCILLATOR STRENGTH OF THE VIOLET SYSTEM OF CN
 J. Chem. Phys. 36, 399 (1962)
 The electron bombardment of HCN to produce the emission spectrum of CN
 is described. The oscillator strength of the $\text{B } ^2\Sigma$ state is determined
 from a direct measurement of the spontaneous radiative lifetime.
180. D. E. Paul and F. W. Dalby
 KINETICS OF DISAPPEARANCE OF THE CN RADICAL FORMED FROM C N_2
 J. Chem. Phys. 37, 592 (1962)
 The flash photolysis of C_2N_2 to produce CN radicals is utilized in a
 kinetic study of the rate of disappearance of CN radical in cyanogen,
 cyanogen chloride, hydrogen, and hydrocarbons. The emission spectrum
 of the CN radical is found to arise from a fluorescence of the CN
 radical and not from formation of radical in its excited state.
181. A. E. Douglas and P. M. Routley
 ON THE SPECTRA OF THE CN^+ AND CN MOLECULES
 Astrophysical Journal 117, 461 (1953)
 The spectra of CN^+ and CN observed from C_2N_2 in a helium discharge tube
 is reported. The band origins and rotational constants of $^1\Sigma - ^1\Sigma$
 transition of CN^+ are listed and two new band systems of neutral CN,
 occurring in the same region as the CN^+ , are identified.

182. R. L. Brown and H. P. Broida
SPECTRAL STUDY OF ACTIVE NITROGEN FLAMES EXHIBITING CN "TAIL" BANDS
J. Chem. Phys. 41, 2053 (1964)

Flames of active nitrogen and simple chlorinated hydrocarbons are reported to exhibit several zones which can be defined by their differences in intensity and spectra. One zone has been found to exhibit that emission which arises from the $B^2\Sigma$ state of CN. The mechanism of its occurrence is postulated.

183. R. N. Dixon and R. W. Nicholls
AN EXPERIMENTAL STUDY OF THE BAND INTENSITIES IN THE CN RED SYSTEM
Can. J. Phys. 36, 127 (1958)

Experimental band intensities are reported for the CN red system obtained from an active nitrogen - carbon tetrachloride source.

184. E. A. Ballik and D. A. Ramsay
GROUND STATE OF THE C_2 MOLECULE
J. Chem. Phys. 31, 1128 (1959)

The rotational and vibrational analysis of C_2 band system as observed in the near infrared spectrum of the emission from a carbon furnace indicate that the $3\Sigma_g^-$ state is the ground state of C_2 in the gas phase.

185. E. A. Ballik and D. A. Ramsay
THE $A' 3\Sigma_g^- \rightarrow X' 3\Pi_u$ BAND SYSTEM OF THE C_2 MOLECULE
Astrophysical Journal 137, 1 (1963)

The detail of the vibrational and rotational lines of the infrared band system of the C_2 molecule is presented and a possible mechanism is advanced to explain the presence of the C_2 Swan bands and absence of the C_2 Phillips bands in cometary spectra.

186. E. A. Ballik and D. A. Ramsay
AN EXTENSION OF THE PHILLIPS SYSTEM OF C_2 AND A SURVEY OF C_2 STATES
Astrophysical Journal 137, 84 (1963)

Nine new bands of the Phillips system of C_2 are presented and measurements on three other bands are extended to higher J values, with new molecular constants evaluated for both states. A general summary of molecular constants for all known states of C_2 and a diagram of the potential curves are given also.

187. V. J. DeCarlo
STUDY IN COMETARY ASTROPHYSICS
NASA Contractor Report, National Aeronautics and Space Administration,
Washington, D. C., July 1964

C_2 emission observed from the vacuum ultraviolet photolysis of low-pressure methane and acetylene is reported to coincide with the Swan bands observed in cometary spectra. A second investigation of the ultraviolet photolysis of ice (H_2O) produced unidentified and unreproducible emission bands and continuum, each occurring between $\sim \lambda$ 4000-4700.

188. L. J. Stief, V. J. DeCarlo and R. J. Mataloni
VACUUM ULTRAVIOLET PHOTOLYSIS OF ACETYLENE
Melpar, Inc., Falls Church, Va., November 1964, (submitted to J. Chem. Phys. for publication)

In a study initiated by a program in cometary astrophysics, the photolysis of acetylene at the krypton and xenon resonance lines is described. Evidence is presented for the production of a long-lived excited state of acetylene which at low pressure leads to the formation of the excited C_2 . The spectra of the C_2 emission at the krypton and xenon lines is consistent with the Swan bands previously observed in cometary spectra. An excited-molecule mechanism for the photolytic reactions is postulated.

189. L. J. Stief and V. J. DeCarlo
ORIGIN OF THE $C_2(A^3\Pi_g) \rightarrow C_2(X^3\Pi_u)$ EMISSION IN COMETS
Melpar, Inc., Falls Church, Va., November 1964 (submitted to Nature for publication)

From the results of laboratory investigation, it is postulated that the C_2 Swan bands observed in cometary spectra are due to the photodissociation of acetylene or an acetylene-type molecule.

190. G. V. Marr
COMBUSTION STUDIES OF ASTROPHYSICAL SIGNIFICANCE. II. A SURVEY OF
CHEMICAL KINETICS FOR PREMIXED HYDROCARBON/OXYGEN FLAMES
The University of Western Ontario, London, Ontario, Canada, July 1, 1956
AD 110 208

The trend of possible reaction processes thought to be occurring in premixed hydrocarbon/oxygen flames is outlined as an aid in the study of reaction processes occurring in astrophysical sources such as comets, etc. The collision processes involved in conventional kinetics are applied to combustion processes. The relevant parameters are defined and an example of the analysis of the steady state departure from thermal equilibrium is given for an idealized flame. The available techniques for the analysis

of the reactions occurring are outlined and considered in the postulation of probable reaction mechanisms which are capable of forming the excited C_2 , CH, HCO, and OH free radicals in premixed hydrocarbon flames.

191. R. G. Bennett and F. W. Dalby
EXPERIMENTAL OSCILLATOR STRENGTH OF COMET-TAIL SYSTEM OF CO^+
J. Chem. Phys. 32, 1111 (1960)

The electron bombardment of CO is utilized to produce the emission spectra of the comet-tail system of CO^+ and to measure the radiative lifetimes of its upper electronic state.

192. D. Robinson and R. W. Nicholls
INTENSITY MEASUREMENTS OF THE CO^+ COMET TAIL, AND THE $BO \alpha$ and β MOLECULAR BAND SYSTEMS
Proc. Phys. Soc. 75, 817 (1960)

The photoelectric measurement of the relative band intensities of the comet tail system ($A^2\Pi - X^2\Pi$) of CO^+ and the $BO \alpha$ and β molecular band systems is reported. The study is a part of a program for the establishment of intensity and transition probability data for molecular band systems of astrophysical, aeronautical, and combustion interest.

193. R. W. Nicholls
TRANSITION PROBABILITIES OF MOLECULAR BAND SYSTEMS
The University of Western Ontario, Department of Physics, London, Canada, June 1962
N631-18009

Franck-Condon factors calculated to high vibrational quantum numbers are presented for vacuum ultraviolet transitions in N_2 , N_2^+ , O_2 , CO, and CO^+ .

194. H. I. S. Ferguson, R. W. Nicholls and L. Herman
EXCITATION OF THE FIRST NEGATIVE SYSTEM OF O_2^+ BY PROTON BEAM IN AIR AND OXYGEN
Colloq. Spectros. Intern. 9th, Lyons, 1961 2, 60-83 (1962)

An account is given of the excitation of the bands of the first positive system of O_2^+ by a beam of 40 KeV protons. Experiments with nitrogen, acetylene, and water vapor are also reported. The experiments indicate that a direct excitation occurs with charge transfer.

195. D. Robinson and R. W. Nicholls
INTENSITY MEASUREMENTS OF THE O_2^+ SECOND NEGATIVE, CO ÅNGSTRÖM AND
THIRD POSITIVE, AND NO γ AND β MOLECULAR BAND SYSTEMS
Proc. Phys. Soc. 71, 957 (1958)

In an effort to obtain intensity measurements for band systems of astro-physical interest, the relative band intensities are reported for the second negative system of O_2^+ , the Ångström and third positive systems of CO, and the γ and β systems of NO.

196. R. G. Turner and R. W. Nicholls
AN EXPERIMENTAL STUDY OF BAND INTENSITIES IN THE FIRST POSITIVE SYSTEM
OF N_2 , Can. J. Phys. 32, 468 (1954)

Vibrational transition probabilities are interpreted from the integrated intensities of 52 bands of the N_2 first positive system.

197. R. G. Turner and R. W. Nicholls
AN EXPERIMENTAL STUDY OF BAND INTENSITIES IN THE FIRST POSITIVE SYSTEM
OF N_2 , Can. J. Phys. 32, 475 (1954)

Band intensities of the first positive system of nitrogen are used together with theoretical transition probabilities to determine the dependence of the electronic transition moment on the internuclear separation.

198. L. V. Wallace and R. W. Nicholls
THE INTERPRETATION OF INTENSITY DISTRIBUTIONS IN THE N_2 SECOND POSITIVE
AND N_2^+ FIRST NEGATIVE BAND SYSTEMS
J. Atm. Terr. Phys. 7, 101 (1955)

The variation of the electronic transition moments is compared with the observed internuclear separations, and the effect of this variation upon the array of vibrational transition probabilities is assessed.

199. R. G. Bennett and F. W. Dalby
EXPERIMENTAL DETERMINATION OF THE OSCILLATOR STRENGTH OF THE FIRST
NEGATIVE BANDS OF N_2^+ , J. Chem. Phys. 31, 434 (1959)

Investigation of the electron bombardment of N_2 has led to the determination of the radiative lifetime of the upper state of the λ 3914 transition of N_2^+ and its corresponding oscillator strength. The radiative lifetime of the upper state of the λ 3371 transition of the second positive system of N_2 is found to depend on the conditions of excitation.

200. J. A. Glasel
THE BOMBARDMENT OF SOLID D_2O BY LOW-ENERGY ELECTRONS UNDER ASTRONOMICAL CONDITIONS
Proc. Nat. Acad. Sci. 48, 491 (1962)

The rate of production of D_2 from the electron bombardment of solid D_2O is measured with a helium mass spectrometer leak detector in an attempt to assess the effect of astronomical conditions on simple molecules in condensed forms.

201. R. Berger
THE PROTON IRRADIATION OF METHANE, AMMONIA, AND WATER AT $77^\circ K$
Proc. Nat. Acad. Sci. 47, 1434 (1961)

Low-temperature mixtures bombarded with 12-MeV protons to produce acetone, urea, and acetamide are described. The significance of this reaction is presented through postulated processes to explain the presence of NH_3 and CO_2 in comets.

202. R. G. Bennett and F. W. Dalby
EXPERIMENTAL DETERMINATION OF THE OSCILLATOR STRENGTH OF THE VIOLET SYSTEM OF OH
J. Chem. Phys. 40, 1414 (1964)

The electron bombardment of CH_3OH and H_2O to produce the violet emission system of OH is used in the determination of the radiative lifetime of the $A^2 \pi \rightarrow X^2 \Sigma$ transition of OH and the corresponding oscillator strength.

PLANNED SPACE INVESTIGATION

203. P. Swings
POSSIBLE CONTRIBUTIONS OF SPACE EXPERIMENTS TO COMETARY PHYSICS
Smithsonian Institution Astrophysical Observatory, Cambridge, Mass., 1962
N63-14253

Suggested plans for space investigations of comets are presented and include discussions of proposed far ultraviolet observations, artificial comets, an orbiting artificial cometary nucleus, and a comet probe. A review of the physical characteristics and past astronomical observations of the spectra of comets is also discussed.

204. D. L. Roberts
THE SCIENTIFIC OBJECTIVES OF DEEP SPACE INVESTIGATIONS. COMETS
IIT Research Institute, 10 West 35th Street, Chicago, Ill., March 9, 1964
N64-19569

Deep space measurements which can provide useful data on comets are discussed along with a description of the comets of interest and the planned space missions.

205. H. C. Corben
REMARKS ON A COMET PROBE
Space Age Astronomy, p. 380, Academic Press, New York, N. Y., 1962

The requirements for launching a comet probe are given in a brief and preliminary assessment.

206. COMET INTERCEPT STUDY
Space Technology Laboratories, Inc., Redondo Beach, California
N63-16229

The study of the requirements and feasibility of a comet intercept mission includes a compilation of the properties of 31 short-term comets, the determination of the injection energies for each of the comets at a suitable launch period, the calculation of the distance of the comet from the earth at intercept, computation of the transit and flight times, determination of necessary guidance requirements, suggestions of possible scientific instruments, and an assessment of the capabilities of available boosters.

207. FAR INTERPLANETARY AND INTERSTELLAR PROBES
Space/Aeronautics, January 1964, p. 98

The programs and probes planned for interplanetary and interstellar investigation are discussed. A Mariner-type craft is stated to be intended for cometary missions, which will probably not be possible before the late 60's or during the 70's. The primary obstacle to a cometary probe is reportedly more precise guidance equipment.

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